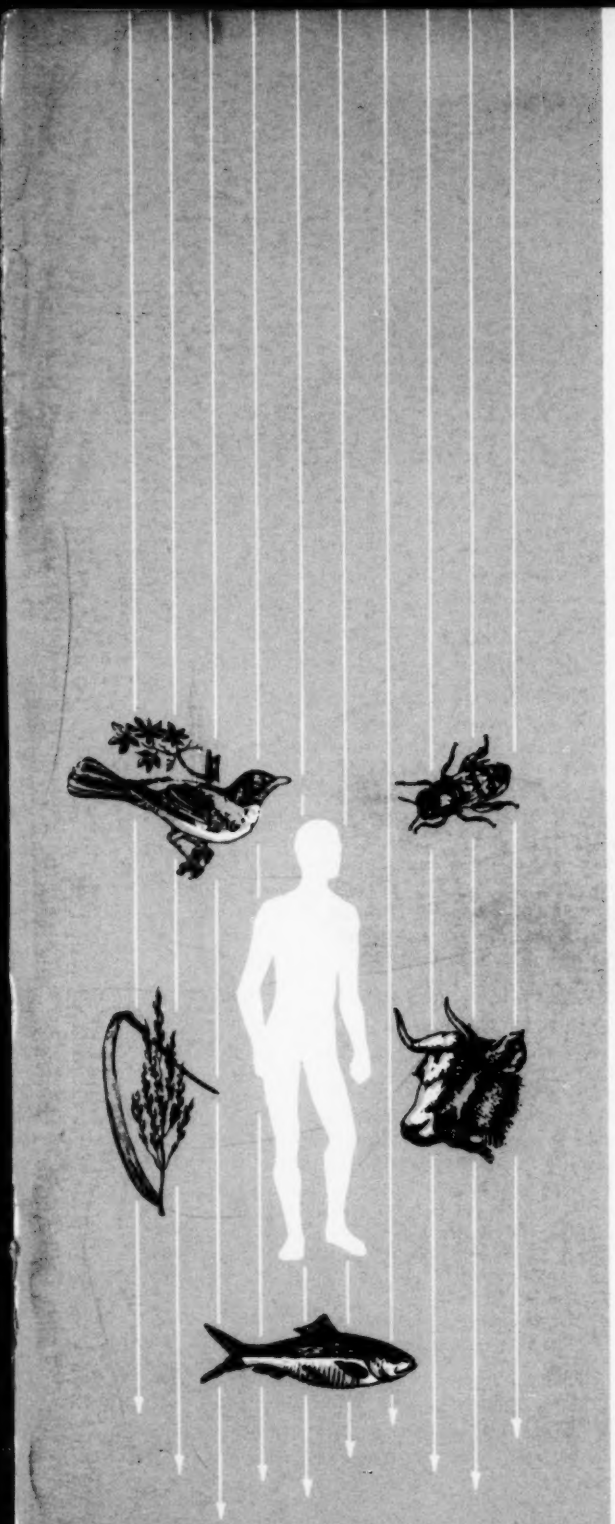

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PESTICIDES IN PEOPLE

Blood Organochlorine Pesticide Levels in Virginia Residents

Francis D. Griffith, Jr.,[1] and Robert V. Blanke [2]

ABSTRACT

This study attempts to establish 1972 baseline levels for 31 organochlorine pesticides and industrial chemicals in postmortem human whole blood in Virginia. These pesticides and industrial chemicals have been detected previously in other parts of the food chain and environment.

In the present study DDT and its metabolites, DDE and TDE, were detected most frequently and at highest levels. DDT and DDE tended to appear more frequently as people grew older although TDE levels remained constant. Dieldrin and lindane showed peak levels in the middle age group.

Analyzing distribution of pesticides in blood by sex showed that females had higher levels of lindane and dieldrin and males had higher levels of DDT, DDE, and TDE. Analyzing racial distribution showed blacks with higher levels of DDT, TDE, and DDE and indicated little difference from whites for lindane and dieldrin. Higher levels were found in Richmond and Norfolk than in the Fairfax and Roanoke regions.

Introduction

This study attempts to establish 1972 baseline levels of organochlorine pesticides in human whole blood in Virginia. It follows by 6 to 12 months the completion of a basic study by the Virginia Department of Agriculture and Commerce (*1*) required by the Virginia General Assembly (*2*) on the occurrence of economic poisons in the environment. Until now, little human monitoring has been done nationally and no studies have been performed on the population of Virginia.

Pesticides which have been detected in the lower part of the food chain and the environment are those most likely to occur in human blood. The study tested for hard organochlorine pesticides as well as some of their alternatives, such as methoxychlor and endosulfan, and some fungicides, such as captan. Polychlorinated biphenyls (PCB's), manufactured as industrial chemicals since the late 1920's, have worked their way through the environment to become manifest in eggs, poultry, fish, beef, packed cereal, and water. Another reason for monitoring PCB's is that several estuaries in Virginia have been contaminated with heavy industrial discharges.

Postmortem blood was selected as the specimen to be examined for the following reasons:

Collection techniques and consent requirements from living patients residing in geographically different regions of the State required facilities beyond authors' control.

Future monitoring can most conveniently be performed on postmortem material; the existing statewide Medical Examiner's system provides a ready mechanism for specimen collection.

Four centers throughout Virginia are assigned to collect specimens from subjects varying widely in age, sex, race, residence, and occupation and make retrievable computer records available on each case.

Similar studies in other areas have used postmortem material (*3*).

The disadvantage of postmortem blood is that it differs from blood of living patients. Some decomposition has occurred, clotting factors are altered, intracellular and extracellular distribution of diffusible substances are altered, and the ratio of formed elements to serum may be modified.

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[2] Department of Pathology, Medical College of Virginia, Richmond, Va.

Sampling Procedures

Blood samples were taken by pathologists in the four regions of the Office of the Chief Medical Examiner: Richmond, Roanoke, Norfolk, and Fairfax. The choice of samples for analysis was based on availability. Variables such as age, race, sex, occupation, residence, and cause of death were not considered initially. Deaths had resulted from trauma, violence, or suspicious, unusual, or unnatural causes; during imprisonment; without medical attendance; suddenly, to a victim who had been in apparent good health; or following surgical or anesthetic procedures (*4*).

Pathologists were requested to take blood within 24 hours after death, although samples drawn as late as 72 hours after death were accepted. Samples were drawn from the heart and placed in 15-cc tubes containing 120 mg sodium fluoride and 45 mg potassium oxalate. To the tube was attached a label bearing the name and address of the deceased, date of death, and the Medical Examiner's signature. In Richmond the tubes were sealed and refrigerated until analysis. In the other regional offices, the tubes were sealed, mailed to Richmond in cardboard containers, and refrigerated upon arrival. After analysis samples were frozen at −25° C for future use.

Analytical Procedures

Aldrin and dieldrin have been extensively used throughout Virginia in recent years. Thus analytical procedures, especially the extraction step, were keyed to the recovery of dieldrin (*5*), which has been detected more frequently in the food chain than has DDT and is five times more toxic to rats and mice on an LD_{50} basis (*6*).

EXTRACTION

The whole-blood extraction procedure was a modification of the sulfuric acid method of Henderson, De Boer, and Stahr used in the 1972 Association of Official Analytical Chemists (AOAC) collaborative study for multiresidues in whole blood (*7*). This method was chosen because sulfuric acid released bound pesticides and sulfonated and removed some of the unsaturated interferences (*8*). Two ml whole blood was pipetted into a 50-ml centrifuge tube; 1.5 ml 60 percent H_2SO_4 was added and mixed on a vortex mixer for 5 seconds; a second 1.5 ml 60 percent H_2SO_4 was added and mixed for 10 seconds; and 2 ml 60 percent H_2SO_4 was added and mixed for 30 seconds. Samples were then cooled for several minutes. Pesticides were extracted with 3 ml 9:1 pesticide-grade hexane:acetone. Samples were mixed 20-30 seconds on a vortex mixer and then centrifuged at 2000 rpm for 10 minutes. The hexane-acetone layer was removed with a disposable capillary pipette and the pesticide solvent layer was put into a 13-ml Kontes graduated centrifuge tube. Hexane-acetone extraction was repeated twice more. All three solvent layer extractions were combined in the same tube. The solvent was concentrated to 0.5 ml by using a gentle stream of clean dry nitrogen on the surface of the extract.

ANALYSIS

Gas-liquid chromatographic (GLC) determinations were performed as described by Griffith and Blanke at the 87th AOAC Annual Meeting (*9*). Samples were run on a Dohrmann Model 2468 gas chromatograph with a microcoulometric gas titrating system (GTS-20) for halogens. Confirmations were made on a Micro-Tek GC-2000-R gas chromatograph equipped with a tritium foil electron-capture detector.

The column used in the microcoulometric system was a 6-ft-by-4-mm-ID glass column packed with 5 percent OV-210 on 80/100 mesh Gas-Chrom Q. The temperature was programmed from 210° to 234° C at 2° C/min. The column used in the electron-capture system was a 6-ft-by-4-mm-ID glass column packed with 4 percent SE-30/6 percent QF-1 on 80/100 mesh Supelcoport. The temperature was isothermal at 205° C. Carrier gas for both systems was nitrogen. Flow through the OV-210 column was 90 ml/min.; flow through the SE-30/QF-1 column was 120 ml/min.

Qualitative results were based on the relative retention of aldrin to the retention of the pesticide in question. Quantitation of pesticides was based on peak area using a disc integrator.

Recovery data were obtained for all compounds discussed. Most analyses were single determinations because precision experiments showed no improvement with triplicate analyses. The desired minimum detectable recovery for all pesticides was 1 ppb. Alpha BHC, lindane, heptachlor, aldrin, heptachlor epoxide, CIPC, and dieldrin were recovered at the 1 ppb level; the limit of detection for DDE, DDT, TDE, dacthal, endrin, endosulfan, and atrazine was 2 ppb. Recoveries for chlordane, dicofol, folpet, captan, chloropropylate, PCNB, carbophenothion, phosphamidon, methoxychlor, and toxaphene varied between 10 and 40 ppb. The minimum detectable amount for PCB's (Aroclor 1221, 1232, and 1242) and PCN's (Halowax 1099) was 100 ppb because of interference from the background of the blood extract. PCB's (Aroclor 1254 and 1260) and PCN (Halowax 1014) had later eluting fractions that did not overlap the backgrounds of the blood extracts; hence the minimum detectable amounts for these chemicals was 50 ppb.

Results and Discussion

When all cases examined in this study were grouped by age (Fig. 1) a normal distribution was apparent, with the majority of samples in the 41- to 60-year age group. The mean ($\bar{x}$) age was 45.98 years. The age distribution in the Richmond and Fairfax regions followed this pat-

tern but distribution showed a majority in the 21- to 40-year age group in the Norfolk and Roanoke regions.

The mean age of Virginia residents in 1972 was 26.8 years; the mean age at death was 68.0 years. The Norfolk region showed a slightly younger living population of 24.2 years. Richmond and Roanoke residents averaged 28.3 and 30.2 years, respectively. The mean age of Fairfax residents and the mean age at death of residents of the other regions are unknown (*10*). Thus the population included in this study represents an older group than the average living Virginia resident but a younger group at death than that which occurs normally.

Sex and race distributions also deviated from the average population (Fig. 2). The racial distribution of the population examined showed a ratio of three whites to two blacks. In the Richmond and Norfolk regions, the racial distribution was 1:1, but whites represented a majority of those samples from the Fairfax and Roanoke regions. The male:female distribution was about 3:1 in all four regions of the State.

The male:female ratio throughout Virginia is about 1:1 and the average white:black distribution is 4:1. Thus data from the present study represent a greater proportion of males and blacks than is typical of the State's population (*10*). If all data from this study are averaged, the resulting baseline of pesticide levels would be misleading. However, when results in each group are taken on the basis of age, sex, race, and geographical residence, they should be comparable to those in corresponding living groups. Similar techniques are commonly used to evaluate data derived from mortality tables (*11*).

On a statewide basis, 15 pesticides and industrial chemicals were positively identified. Ten of these are shown in Figure 3. The remaining five did not occur in enough samples to be included. The most frequently detected pesticides were DDT and its metabolites, dieldrin, lindane, and alpha BHC. Less frequently detected were methoxychlor, heptachlor epoxide, CIPC, and PCB's. Captan was detected at levels of 20 to 30 ppb, and carbophenothion was found at levels of 8 to 60 ppb in two samples each. Chloropropylate, PCNB, and endrin were each detected in one sample at 27, 15, and 5 ppb, respectively.

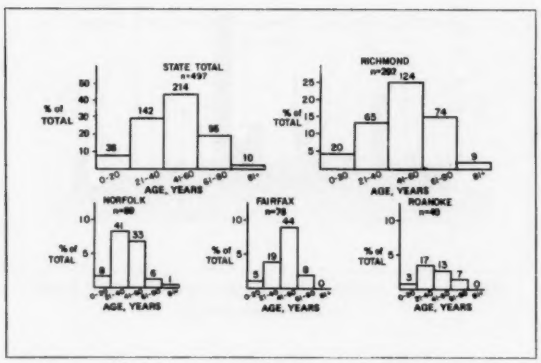

FIGURE 1. *Age distribution of humans sampled for pesticide residues*

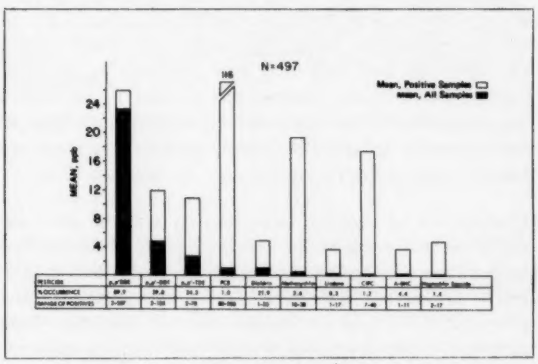

FIGURE 3. *Organochlorine residues detected in human blood*

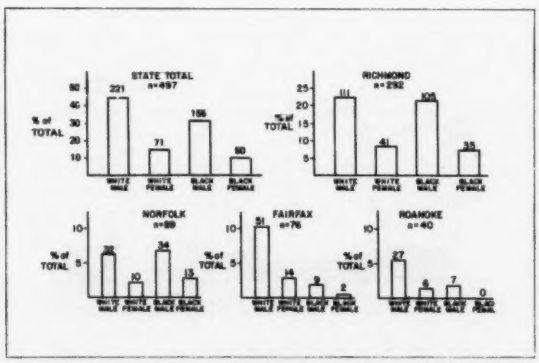

FIGURE 2. *Sex and race distribution of humans sampled for pesticide residues*

Of equal importance are the 16 pesticides and industrial chemicals that were not detected. Chlordane was not detected; nor were the herbicides atrazine and dacthal, probably because of their rapid degradation. Toxaphene, the PCN's, and most PCB's did not appear.

Heptachlor and aldrin were not found, although their metabolites dieldrin and heptachlor epoxide were. The latter occurred in only 1.4 percent of the samples studied at an average concentration of 0.06 ppb. This is a significant decrease from the mid-sixties when that metabolite was first detected in milk (*12*). The current findings may indicate that milk is no longer a significant

source of PCB contamination, although such a conclusion could be verified only through extensive research into several areas, including the dietary habits of subjects whose blood was sampled.

Methoxychlor, CIPC, and PCB's were detected in a small percentage of samples with wide differences between frequency and concentration means (Fig. 3). Authors interpret this to indicate that they do not have widespread distribution and, when detected, probably indicate recent exposure.

Concentrations and frequencies of DDE and DDT in blood by age showed similar patterns (Fig. 4,5). On a statewide basis, higher concentrations and occurrences were noted with advanced age. On a regional basis, Richmond and Norfolk had generally higher DDE and DDT concentrations and occurrences than had Fairfax and Roanoke. Distribution of TDE by age differed from DDT and DDE: it was fairly uniform except in the Norfolk region (Fig. 6). Average concentrations were higher in the 0- to 20-year age group although percent occurrence was lower in this group.

Dieldrin and lindane occurred less frequently but generally showed peak levels at middle age (Fig. 7,8). In the case of lindane, no positive cases were found among the very old and only one was detected in the very young. Dieldrin distribution was skewed to an earlier age group in the Roanoke and Norfolk regions than in the other two. In Norfolk, dieldrin levels were generally lower except in the very young.

Distribution of detected pesticides by sex and race did not show any remarkable trends (Fig. 9). Females had higher levels of lindane and dieldrin; males had higher levels of DDT, DDE, and TDE. Blacks had higher levels of DDT and its metabolites but displayed little difference from whites in lindane and dieldrin concentrations. Higher pesticide levels and greater percent occurrences were found in Richmond and Norfolk than in Fairfax and Roanoke.

No correlations between residue levels and occupation could be considered because of the wide variation in occupations listed on Medical Examiner's certificates. Many people over 60 were listed as retired; others were unemployed.

Although some pesticides are known to alter microsomal enzyme activity and, consequently, drug metabolism (*13*), the low number of deaths by barbiturate overdosage prohibited observation of any relationship between pesticide levels and drug levels.

In no case was pesticide poisoning considered the cause of death. Had it been, the pesticide would have been present in much higher levels, as observed in published findings on known overdosages and exposures (*14*).

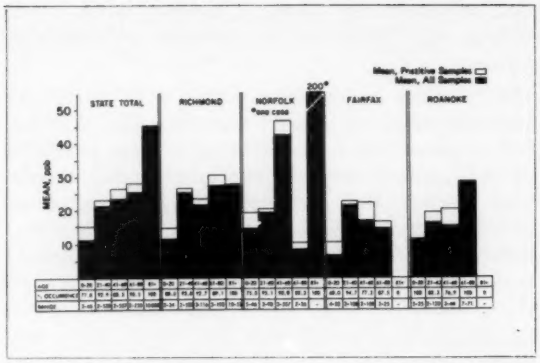

FIGURE 4. *DDE residues detected in human blood by age distribution*

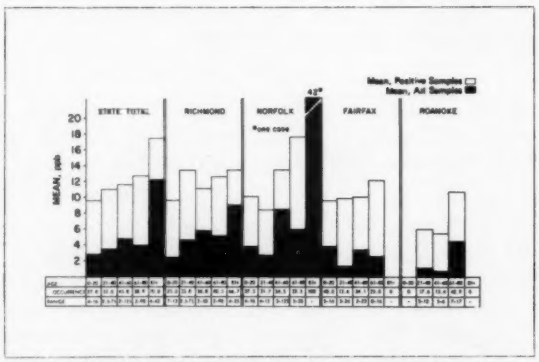

FIGURE 5. *DDT residues detected in human blood by age distribution*

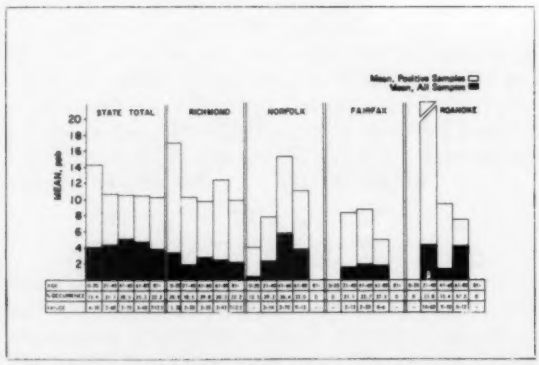

FIGURE 6. *TDE residues detected in human blood by age distribution*

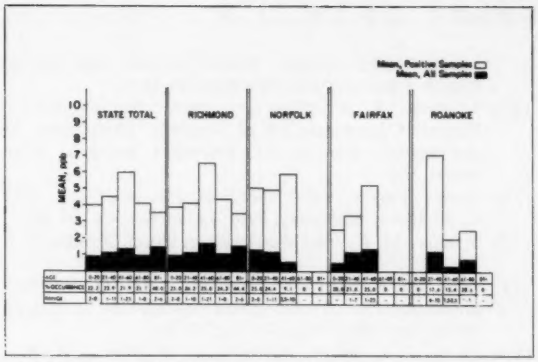

FIGURE 7. *Dieldrin residues detected in human blood by age distribution*

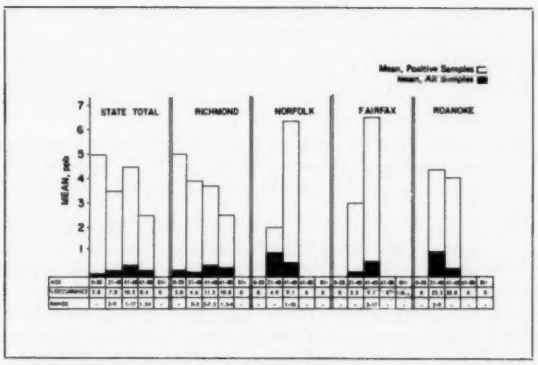

FIGURE 8. *Lindane residues detected in human blood by age distribution*

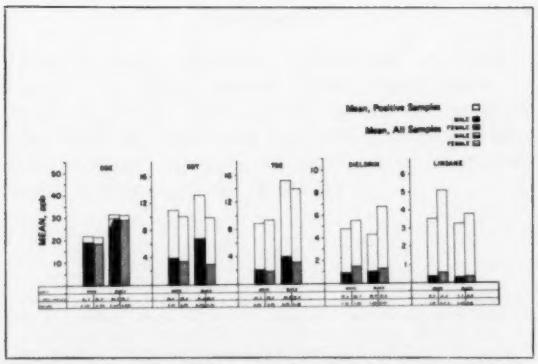

FIGURE 9. *Pesticide residues detected in human blood by sex and race distribution*

Conclusions

Pesticide levels in human blood of Virginia residents generally coincide with levels found in other studies. Exceptions probably stem from improvements and refinements in analytical methods, differences in time periods during which subjects were exposed to environmental pollutants, and variations in sample populations. Levels of DDT and its metabolites are very similar to those reported by Dale et al. in Georgia (*15*), slightly higher than those obtained by Davis and Edmundson et al. in Florida (*16,17*) and by Watson et al. in Idaho (*18*), and lower than results reported by Keil et al. in South Carolina (*19*). The percent occurrence of DDT and its metabolites found in this study is much lower than that reported by Watson et al. (*18*). This may parallel the decline of DDT residues in lower parts of the food chain in Virginia which was first noticed in 1970. The slightly higher occurrence of dieldrin in samples from the central region of Virginia coincides with the frequency with which this pesticide is detected in the food chain. Most samples of water from the James River basin contain low levels of dieldrin. Lindane occurred more frequently than had been anticipated from previously reported pesticide residue analyses (*1,20*). This may result from the common use of lindane in commercial vaporizers and its presence in cigarette smoke (*21*).

Differences in residue levels and percent occurrence by sex were not striking. Racial differences observed for all pesticides can be accounted for by various socioeconomic factors discussed by Davis et al. (*16*).

Residue levels detected did not indicate a health hazard from environmental contamination by pesticides in Virginia communities (*22*). Although none of the differences are statistically significant when applying the chi-square test, hopefully the data acquired will establish a baseline for residents of this State. Continuous monitoring should detect significant changes. DDT levels are expected to drop but residues of DDT metabolites may remain relatively constant or decrease at a lower rate. Dieldrin concentrations will probably remain relatively constant or decrease at a lower rate than DDT.

Future studies should be expanded to include additional pesticides and specimens such as adipose tissue and liver to better define overall pesticides body burden. It would also be useful to compare results in this study with a limited number of blood specimens from living patients of similar age, sex, race, and geographic origin to determine the suitability of postmortem blood as a sample for monitoring pesticide residues in humankind.

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PESTICIDES IN WATER

Fate of Copper in Ponds[1]

A. W. McIntosh [2]

ABSTRACT

Treatments of 3 ppm copper sulfate ($CuSO_4 \cdot 5H_2O$) were applied to two small aquatic systems in Michigan in 1971. To study the pathways of the added copper, samples of water, sediment, aquatic macrophytes, filamentous algae, and fish were collected and analyzed by atomic absorption. Sampling was initiated before treatment and continued up to 4 months in one of the ponds.

Dissolved copper concentrations in water decreased rapidly immediately after treatment and then gradually to background levels. Reduction of dissolved copper may have involved initial precipitation of an insoluble compound, such as malachite, followed by sediment adsorption of soluble copper complexes and copper released from aquatic plants. Levels of copper in sediment increased rapidly at first and gradually later in the study. Aquatic plants and filamentous algae accumulated very high levels of copper. Uptake rates were apparently affected by water temperature and growth stages of the plants. Data indicate that aquatic macrophytes developing in one pond 10 weeks after treatment took up copper from the sediment. Although green sunfish (Lepomis cyanellus) *accumulated copper soon after treatment, levels returned to background later in the study.*

Introduction

Levels of copper generally below 20 ppb are routinely observed in natural waters. When higher values are found in surface waters, it is likely that the metal has been added by copper and brass tubing, industrial effluents, or copper compounds used for control of undesirable aquatic organisms or plants (*1*).

Limited research has been conducted concerning the fate of copper in aquatic systems, including copper pathways in canals and irrigation ditches (*2-4*), bogs (*5*), ponds (*6,7*), and lakes (*8*). In assessing the ecological effects of a heavy metal, components concentrating it must be identified and characterized. Little effort has been devoted to determining the role of these aquatic system components in copper dispersal.

In the present study in which copper sulfate ($CuSO_4 \cdot 5H_2O$) was added to two small ponds in Michigan in 1971, intensive sampling of water, sediment, algae, plants, and fish was conducted for periods of 7 weeks to 4 months to assess the role of each component in copper distribution.

Methods and Materials

STUDY SITE

A circular settling pond about 13.7 m in diameter and 2 m deep served as the study site. Located at the old East Lansing Sewage Treatment Plant, the pond is among a number of sites used by the Michigan State University Department of Fisheries and Wildlife for limnological research. In June 1970 the pond was drained and the bottom was covered with 10 to 15 cm black soil. The system was refilled and left undisturbed while populations of macrophytes and filamentous algae developed.

Early in May 1971 the system was divided with a polyethylene sheet, effectively forming two separate ponds. By June, 100 green sunfish (*Lepomis cyanellus*) had been collected from other sources. They were weighed, marked by fin-clipping, and released into each system. Copper sulfate solutions were prepared in distilled water from commercial grade copper sulfate and applied by hand to the surface of each pond. Application dates and dosages appear in Table 1.

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TABLE 1. *Copper sulfate dosage rates and schedules*

SITE	APPLICATION DATE	DOSAGE, PPM
Pond A	July 12, 1971	3
Pond B	September 26, 1971	3

NOTE: Ponds A and B are halves of one settling pond.

Water chemistry parameters including pH, alkalinity, hardness, and dissolved oxygen were determined throughout the study (Fig. 1,2). Techniques outlined in *Standard Methods for the Examination of Water and Wastewater* (*9*) were used for chemical tests. Duplicate water samples were collected for analysis from the top and bottom quarters of each pond with a Kemmerer water sampler.

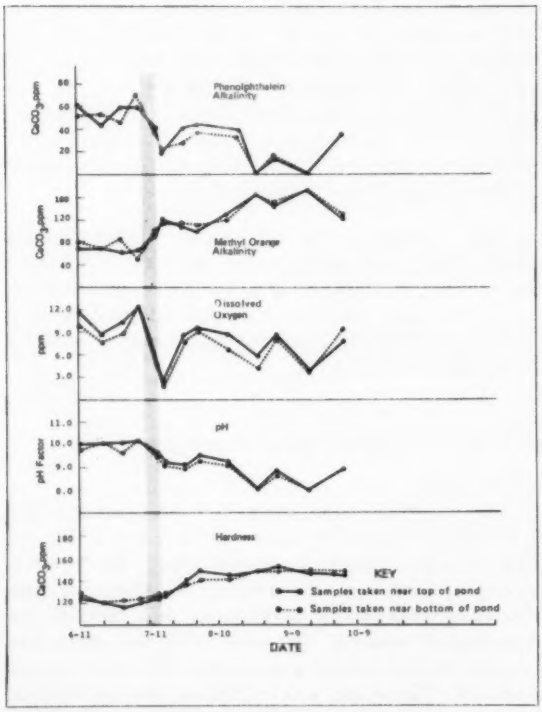

FIGURE 1. *Changes in water chemistry parameters, Pond A*

NOTE: Each point represents average of two samples. Shaded area denotes treatment with 3 ppm copper sulfate.

Sampling and Analysis

Water for copper analyses was collected at three stations established near the outside, middle, and inside of each semicircular pond. A water column was removed with a polyethylene tube and a subsample was collected. Preparation followed procedures outlined in *Methods for Chemical Analysis of Water and Wastes* (*10*). Copper passing through a 0.45-μ membrane filter represented dissolved copper; the fraction remaining on the filter was considered suspended copper.

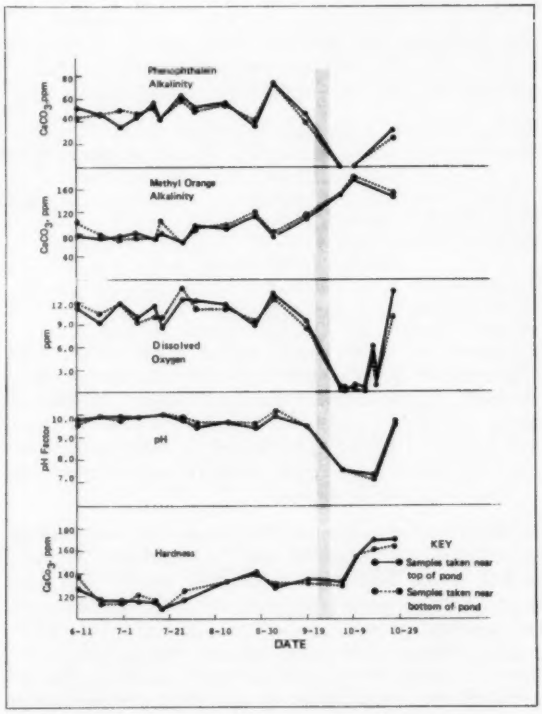

FIGURE 2. *Changes in water chemistry parameters, Pond B*

NOTE: Each point represents average of two samples. Shaded area denotes treatment with 3 ppm copper sulfate.

At each sampling period, two sediment samples were collected with a core sampler and frozen in dry ice. The top 1- 2-in. layer was removed and dried at 100° C for 96 hours. Samples were ground and 5 ml 8N HCl/g sediment was added. This slurry was held at a temperature near boiling for 20 hours, cooled, filtered, and diluted to volume with deionized distilled water.

Plant samples were collected, rinsed in distilled water, blotted, and dried at 100° C for 96 hours. Tissues were digested by adding 10 ml 8N HNO_3 and boiling to dryness. Five ml 6N HCl was then added and the mixture was reheated to dissolve the residue. The solution was filtered and diluted to the desired volume.

Fish were trapped, sacrificed, rinsed in distilled water, weighed, and digested in 5 ml concentrated HNO_3/g fish for 24 hours. The solution was filtered and diluted to volume.

Samples of all components were taken before treatment to determine background levels of copper (Table 2). Samples were collected after treatment for 4 months in Pond A and for 7 weeks in Pond B.

TABLE 2. *Background copper levels in two Michigan ponds, 1971*

Component	Average Concentration, Copper, ppm	Range, ppm	No. Samples
WATER			
Dissolved copper [1]	0.0145	0.00-0.05	38
Suspended copper [2]	0.0357	0.00-0.09	38
Total	0.0502	0.00-0.11	38
SEDIMENTS [3]	27.68	1.08-73.60	51
PLANT TISSUE [3]			
Chara sp.	15.92	6.09-36.70	20
Oedogonium sp.	34.40	12.54-51.68	19
Elodea Nuttallii	26.31	2.33-50.51	28
Potamogeton crispus	26.31	4.69-55.80	20
FISH [4]			
Green sunfish	0.56	0.00-1.64	22

[1] Filtered through 45-μ membrane filter.
[2] Fraction left on membrane filter.
[3] Dry-weight basis.
[4] Whole-body wet-weight basis.

The presence of copper was determined with a Jarrell-Ash atomic absorption spectrophotometer Model 800. Sample concentrations were determined by comparing their readings to those of copper sulfate standards prepared several times during the tests. To insure accuracy, three standards were compared to those of another investigator; the discrepancy was less than 10 percent.

During analyses, uncontaminated samples were spiked with copper to determine percent recovery. Recoveries for plant tissues ranged from 89.9 to 114.4 percent with a mean of 101.2 percent; recoveries from sediments ranged from 94.7 to 120.0 percent with a mean of 109.9 percent.

Reproducibility was determined by reading the same samples on different occasions. When tested with a paired-t test, pairs of readings were not significantly different at the 5 percent level.

Copper added to the ponds accumulated on upper sediment surfaces. Because little downward movement of copper into sediment was expected during the test period, sediment copper values were expressed as weight accumulated on sediment surfaces. Average pretreatment copper concentrations were calculated in μg/g for pond sediment, and total μg copper present in the upper layer was determined for each core sample taken after treatment. The average μg/g pretreatment copper concentration was subtracted from the total μg copper present in the upper layer after treatment to yield μg copper deposited on the upper surface of each core.

Results and Discussion

WATER

Dissolved copper concentrations in Pond A diminished gradually after rapid decline of initial peaks (Fig. 3). High concentrations at stations A1 and A2 shortly after treatment were probably caused by slow dispersal of copper sulfate. Malachite ($Cu_2(OH)_2CO_3$) precipitation, a slow process reaching equilibrium only several days after application (*11*), may have played a large role in the decline.

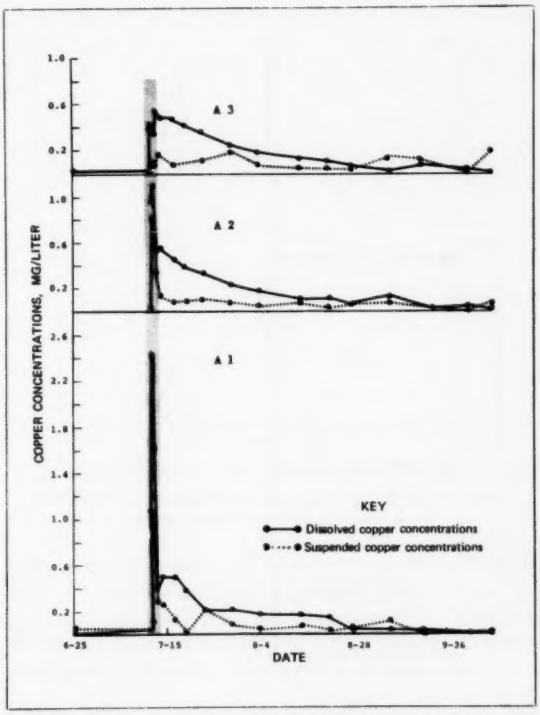

FIGURE 3. *Changes in dissolved and suspended copper concentrations, Pond A, three sites*

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

Levels of organic acids in the range of 4 to 40 ppm carbon in water may increase the amount of metal stabilized in solution by several orders of magnitude (*12*). Ten sediment samples from Pond A contained an average of 11 percent organic matter; organic complexes in the overlying water may have slowed the decline of dissolved copper.

Suspended copper levels in Pond A showed no trends. Although an initial peak occurred, concentrations of suspended copper soon declined to background levels (Table 2).

Dissolved copper concentrations in Pond B followed a pattern similar to that of Pond A following treatment (Fig. 4). Copper levels peaked initially, and subsequently decreased. However, sudden increases in dissolved copper occurred at all stations about 3 weeks after treatment. This rise, coinciding with the decomposition of extensive masses of *Chara*, was probably caused by release of copper from its tissues. After these secondary peaks, a rapid decrease in dissolved copper levels occurred. Detrital particles from the decomposing *Chara* may have aided in removing copper from solution.

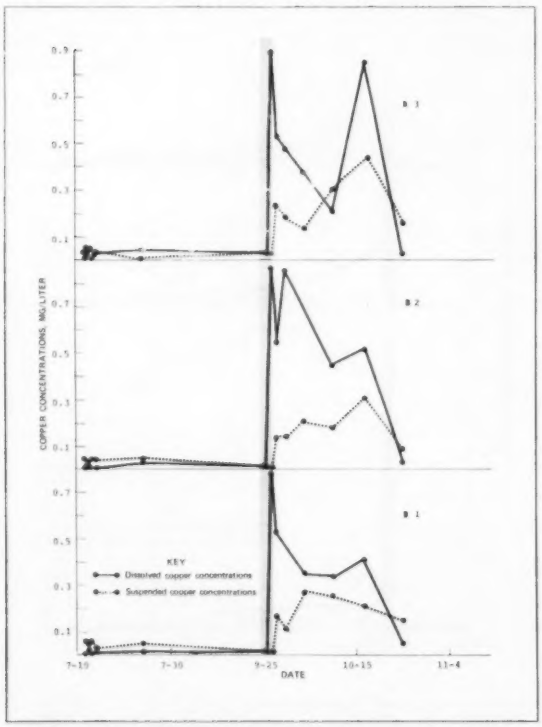

FIGURE 4. *Changes in dissolved and suspended copper concentrations, Pond B, three sites*

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

Suspended copper concentrations in Pond B increased slightly after treatment and then rose to levels between 0.3 and 0.5 mg/liter after 21 days. Copper-bearing particles from disintegrating *Chara* may have caused the elevated levels.

In general, a rapid loss of dissolved copper from solution has occurred in most experiments performed in alkaline water (*5,13*). In the present study, significant levels of dissolved copper remained after several weeks, possibly because of copper-containing organic complexes in the pond water.

SEDIMENTS

After treatment in Pond A, copper accumulated in sediment rapidly at first and then gradually (Fig. 5). Precipitation of insoluble compounds probably accounted for the initial increase. Later accumulations may have been caused by gradual adsorption of dissolved copper and of copper released from plants and algae. Although sediments collected copper more quickly in Pond B than in Pond A, overall accumulation patterns of the two ponds were similar. Published research indicates that copper is rapidly adsorbed by pond sediments and that the amount of copper fixed is determined by the amount of organic matter and nature of clay minerals present (*7*). Because sediment in the current study contained a high level of organic matter (11 percent) copper was probably fixed once it reached the bottom.

Evidence indicates that sediment acts as the ultimate repository of copper added to an aquatic system. Precipitation of copper compounds followed by gradual adsorption of copper complexes from water probably occurred in the present study.

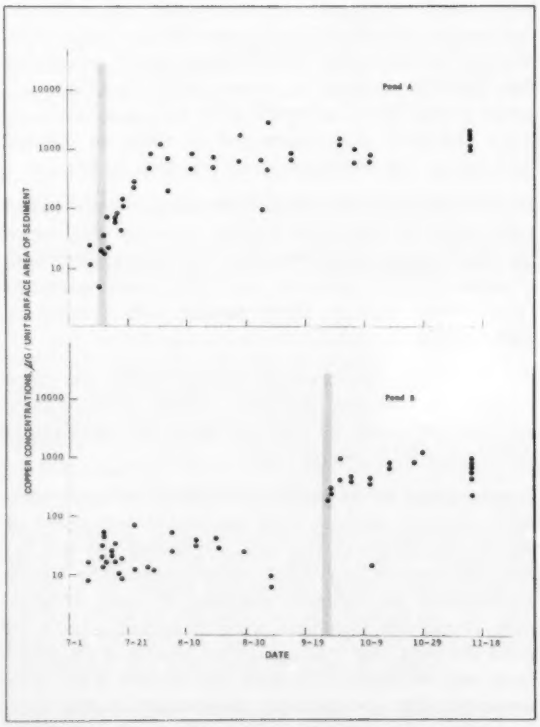

FIGURE 5. *Copper accumulation in sediment surface sampled by core, Ponds A and B*

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

PLANT TISSUES

Plant tissue rapidly accumulated high levels of copper in Pond A (Fig. 6). The ratio of copper concentration in dried tissue to the initial concentration in water after dosage was greater than 3000:1 for the three species present (Table 3).

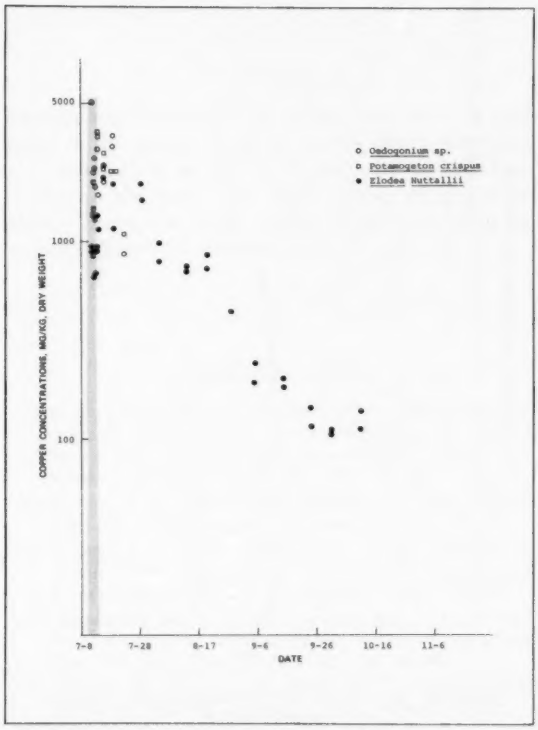

FIGURE 6. *Copper accumulated by plant tissue, Pond A*

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

TABLE 3. *Concentration factors of copper in dried plant tissue relative to theoretical initial concentration in pond water after treatment*

PLANT	COPPER CONCENTRATION RATIO (PLANTS:WATER, PPM)	
	POND A	POND B
Chara sp.	—	1360
Potamogeton crispus	4616	1716
Elodea Nuttallii	3018	3329
Oedogonium sp.	4358	2846

Declining copper concentrations noted in *Elodea* (Fig. 6) may have been caused by loss of copper-bearing tissue by disintegration and an interruption of growth processes and subsequent copper accumulation.

Copper concentrations in macrophytes which developed in Pond A after treatment were slightly above background levels (Fig. 7). Copper concentrations near background levels in water indicate that uptake from sediment may have occurred. These results corroborate those of Bartley, who found that pond weeds in an irrigation canal accumulated residual copper from the hydrosoil (*2*).

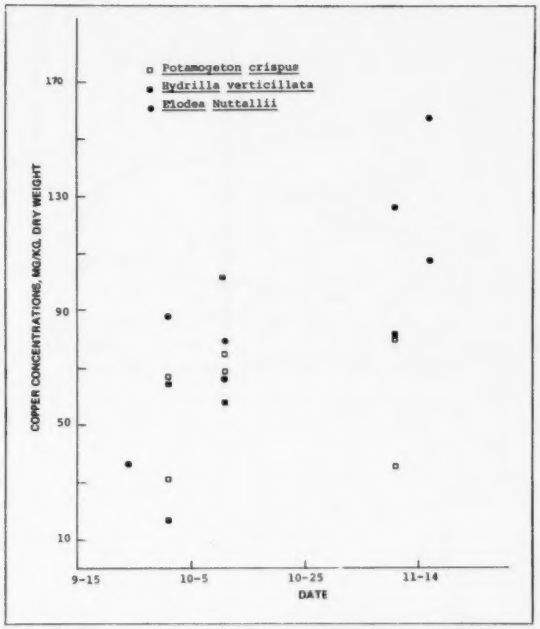

FIGURE 7. *Copper accumulated by plants growing after sulfate treatment, Pond A*

Copper was also taken up rapidly by plants in Pond B (Fig. 8). Residue levels were generally lower (Table 3) and increased more gradually than they did in Pond A. Water temperatures in Pond B, which were 5° C lower than those in Pond A, may have been responsible.

Copper levels in *Elodea* in Pond B were higher than those in either *Potamogeton* or *Oedogonium;* in Pond A, however, *Elodea* had copper concentrations lower than those in the other two species. Uptake may have been related to growth activities; species which grew most rapidly during treatment accumulated highest levels of copper.

The current study shows that aquatic plants are capable of concentrating very high levels of copper. Differences in accumulation between species seemed related to growth conditions of plants. Species growing most rapidly during treatment had highest levels.

FISH

Slight increases in fish whole-body copper concentrations occurred after treatment in both ponds (Fig. 9). Fish in Pond A had levels of about 3 ppm copper 1 week after treatment and again 47 days after treatment.

Levels decreased to the background value of about 0.5 ppm 79 days after treatment. Pond B fish showed copper increases up to about 2 ppm 10 days after treatment; 51 days after treatment residues had decreased to background levels.

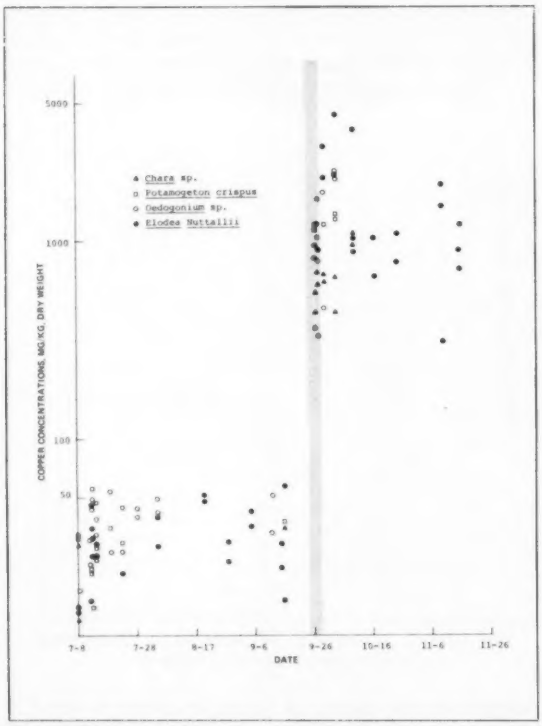

FIGURE 8. *Copper accumulated by plant tissues, Pond B*

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

COMPONENTS OF COPPER DISTRIBUTION

The fraction of applied copper in each major component of Ponds A and B was estimated on each sampling date. Plant values were calculated by estimating the weight of plant masses and total copper accumulated in the masses. Water concentrations included copper in dissolved and suspended states. Weight of copper on the total sediment surface at each sampling time was estimated by multiplying the average copper value of an individual core sample by a factor calculated by dividing total sediment surface area by core surface area.

Figure 10 graphs only water and sediment copper for Pond A because plant tissues always contained less than 1 percent of the total copper applied. A clear relation existed between water and sediment copper fractions in Pond A: a decrease of copper in water with a concomitant increase in sediment copper occurred. The estimated amount of copper in sediment at the end of the experiment was greater than 90 percent of the total applied.

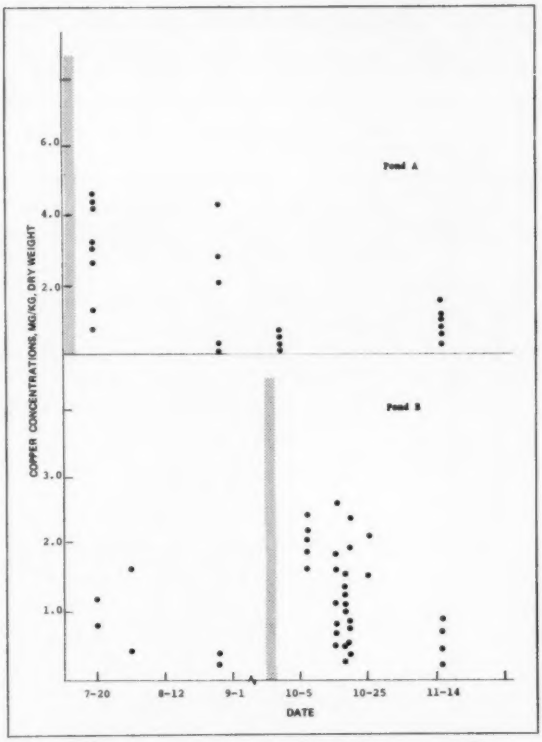

FIGURE 9. *Copper accumulated by green sunfish, Ponds A and B*

NOTE: Shaded area denotes treatment with 3 ppm copper sulfate.

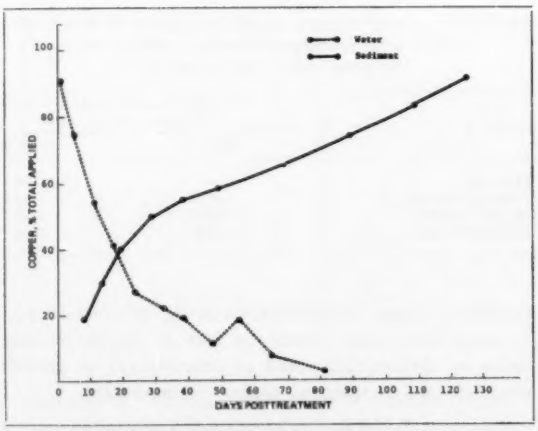

FIGURE 10. *Total applied copper present in water and sediment, Pond A*

Plant tissue, mostly *Chara*, played a significant role in Pond B copper dynamics (Fig. 11). Percentage of copper in plant tissues 14 days after treatment was estimated to be about 10 percent of the total applied. Copper was released shortly thereafter during decomposition. Sediment accumulation followed a pattern similar to that of Pond A. Copper values in the water were influenced by release of copper from dying *Chara* tissue.

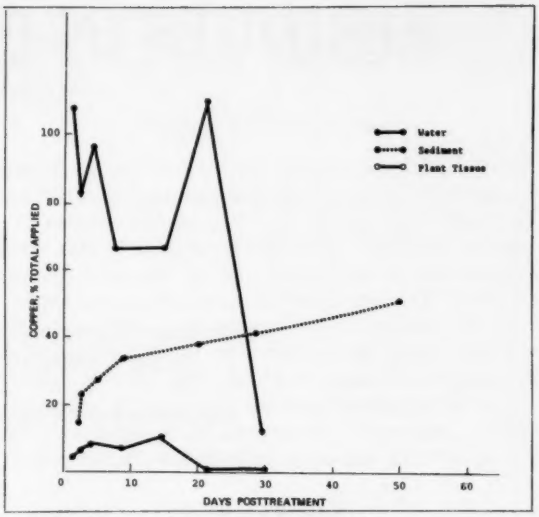

FIGURE 11. *Percent of total applied copper present in water, sediment, and plant tissue, Pond B*

Conclusion

As expected, copper moved rapidly from water to sediment in the ponds observed in this study. However, phenomena such as binding of metals by organic compounds in the water and rapid uptake of metals by aquatic plants and algae cannot be overlooked in assessing dispersal of a metal in aquatic systems.

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RESIDUES IN FOOD AND FEED

Preliminary Survey of Ethylenethiourea Residues in the Canadian Food Supply, 1972

Zigmund Pecka,[1] Patricia Baulu,[2] and Harvey Newsome [3]

ABSTRACT

A preliminary monitoring program was initiated in 1972 to determine ethylenethiourea (ETU) content of the Canadian food supply. Of 167 samples analyzed, 90 were domestic and 77 were imported. Samples were analyzed by electron-capture/gas-liquid chromatography. Thirty-three percent of the samples contained detectable ETU residues; most of these were 0.020 ppm or less. Highest levels, 0.047 and 0.083 ppm, were found in canned spinach and orange peel, respectively.

Introduction

Ethylenebisdithiocarbamates are widely used as fungicides and may, under conditions of aeration (*1*) or cooking (*2*), degrade to ethylenethiourea (ETU). The compound has been identified as a component of commercial ethylenebisdithiocarbamate formulations (*3,4*). Toxicological studies have shown ETU to be goitrogenic (*5*), carcinogenic (*6*), and teratogenic (*7*). In view of these findings, the present survey was conducted in 1972 to establish ETU levels in the Canadian food supply.

Sampling Procedures

A total of 167 samples were analyzed. Of these, 85 were obtained by the Inspection Services of the Quebec Region, Health Protection Branch, and 82 were obtained by the Inspection Services of the Ontario Region. Both domestic and imported products were analyzed: 90 of the former and 77 of the latter. Of the 77 imports, 56 were from the U.S.A., 9 from Mexico, 5 from Holland, 2 from Switzerland, 2 from Chile, 1 from Morocco, 1 from Israel, and 1 from Poland.

For small fruits and vegetables (e.g., grapes, Brussels sprouts, beans), minimum sample size was 3 lb. For medium-size fruits and vegetables (e.g., apples, oranges, potatoes), minimum samples were 3 lb or 10 units. For large commodities (e.g., cabbage, lettuce), a minimum number of 3 was used for each sample. For canned goods, 5 cans of each type were combined to make 1 sample. A 1-lb minimum of cereal or wheat product was obtained for each sample. All samples were cut, blended, and stored in mason jars in a freezer before analysis.

Analytical Procedures

The method of analysis was a modification of one described previously (*8*). Stored samples were thawed and a 5.0-g portion was homogenized with 50 ml absolute ethanol in a Sorvall Omni-Mixer. Solids were removed from the homogenate by filtration through Whatman No. 1 paper using a slight negative pressure and a filtrate diluted to 100 ml with distilled water. Twenty-ml aliquots of the diluted extract were placed in 50-ml round-bottomed flasks, and 0.1 ml benzyl chloride was added. The benzyl chloride had been purified previously by passage through a column of alumina as described by Onley et al. (*9*) for n-bromobutane. After refluxing the contents of the flasks for 30 minutes samples were cooled and transferred to 125-ml separatory funnels with 30 ml distilled water. Hydrochloric acid (1 *N*; 1.0 ml) was added and samples were extracted with two (1 × 10 ml and 1 × 5 ml) solutions of chloroform which were later discarded. Potassium hydroxide (1 *N*; 5.0 ml) was added to the aqueous phase and the s-benzyl ETU was immediately extracted with 10 ml chloroform. Extracts were dried by passage through a small bed of sodium sulfate and placed in 12-ml vials containing 10 µl paraffin oil. Chloroform was removed by evaporation under a stream of nitro-

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gen. By varying nitrogen flow, the rate of evaporation was controlled enough that 1.5 hours or more were required to remove 10 ml. More rapid evaporation sometimes leads to losses of derivative.

Samples were trifluoroacetylated by adding a solution of 10 percent trifluoroacetic anhydride in 0.50 ml benzene and permitting them to react for 15 minutes at room temperature. The solvent was evaporated almost to dryness under a gentle stream of nitrogen and the trifluoroacetylation was repeated with an additional 0.50 ml reagent for 15 minutes. After removal of the solvent, samples were dissolved in 1.0 ml benzene and a 5.0-µl aliquot was analyzed by gas-liquid chromatography (GLC).

GLC was performed on a Varian Aerograph 1400 fitted with a tritium foil electron-capture detector and a 6-ft-by-⅛-in.-ID glass column. The column was packed with 4 percent SE-30, 6 percent QF-1 on Chromosorb W HP and operated at 200° C with a nitrogen flow of 100 ml/min. The injection port and detector were maintained at 220° C. Under these conditions trifluoroacetylated s-benzyl ETU had a retention time of 12 minutes.

ETU, added at levels of 0.05 and 0.10 ppm to 17 commodities, was recovered at a mean of 96.0 percent ± a standard deviation of 8.9 percent. The minimum detectable limit, defined as twice background, was 0.01 ppm. Because of low levels of ETU encountered in the samples, GLC/mass spectral confirmation (*8*) was not attempted.

Results and Discussion

Results of the analyses are presented in Table 1. Of the 167 composite samples analyzed for ETU residues, 112 samples (67 percent) did not contain detectable levels and 55 samples (33 percent) contained residues ranging from 0.01 to 0.15 ppm. Most of the samples (92 percent) contained 0.02 ppm or less ETU. Notable exceptions were some samples of canned spinach with an average of 0.047 ppm and orange peels with an average of 0.083 ppm. Of the 90 domestic samples, 29 composites (32 percent) contained detectable levels of ETU compared to 26 composites (34 percent) of the 77 imported foods containing detectable ETU levels.

Acknowledgments

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TABLE 1. *Ethylenethiourea residues in foods sampled from Quebec and Ontario, Canada—1972*

Food	Type	No. Samples Analyzed	No. Positive Samples	Mean of Positive Samples, ppm	Range of Positive Samples, ppm
Potatoes	Fresh	13	4	0.025	0.010-0.050
Tomatoes	Fresh	10	3	0.020	0.010-0.030
Tomatoes	Canned	5	4	0.018	0.010-0.020
Apples	Fresh	10	4	0.028	0.020-0.050
Lettuce	Fresh	10	3	0.013	0.010-0.020
Carrots	Fresh	9	5	0.010	0.010-0.010
Carrots	Canned	1	0	ND	ND
Green beans	Fresh	4	0	ND	ND
Green beans	Canned	5	2	0.020	0.020-0.020
White kidney beans	Canned	1	0	ND	ND
Cabbage	Fresh	8	1	0.010	ND
Cabbage	Canned	1	0	ND	ND
Sauerkraut	Canned	3	0	ND	ND
Broccoli	Fresh	10	4	0.020	0.010-0.040
Brussels sprouts	Fresh	8	2	0.020	0.020-0.020
Celery	Fresh	7	4	0.015	0.010-0.020
Cherries	Canned	10	0	ND	ND
Spinach	Fresh	7	2	0.025	0.020-0.030
Spinach	Canned	5	3	0.047	0.040-0.050
Cucumber	Fresh	7	1	0.050	ND
Dill pickles	Jarred	3	0	ND	ND
Grapes	Fresh	10	5	0.020	0.010-0.050
Oranges (peel)	Fresh	5	3	0.083	0.030-0.150
Oranges (pulp)	Fresh	5	3	0.020	0.020-0.020
Wheat	Fresh	5	2	0.015	0.010-0.020
Flour	Bagged	3	1	0.040	ND
Puffed wheat	Boxed	1	0	ND	ND
Shredded wheat	Boxed	1	1	0.010	ND
Wheat germ	Boxed	1	0	ND	ND
Wheat germ flakes	Boxed	1	0	ND	ND
Wheat hearts	Boxed	1	1	0.010	ND
Bran flakes	Boxed	1	0	ND	ND
Cereals	Boxed	1	0	ND	ND

NOTE: ND = none detected.
Canned implies use of tin can; jarred implies use of glass jar.

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RESIDUES IN FISH, WILDLIFE, AND ESTUARIES

Pesticide and Mercury Residues in Commercially Grown Catfish[1]

A. B. Crockett,[2] G. B. Wiersma,[2] H. Tai,[3] and W. Mitchell[3]

ABSTRACT

In 1970, 54 commercial catfish farms in Arkansas and Mississippi were sampled for pesticide and mercury residues. Pesticide residues above FDA action levels were detected in 15 percent of the fish samples. Data on residues in sediment, fish feed, and source water suggest that fish were not being contaminated from these sources. Average fish residue per county was, however, strongly correlated with the percent of total acres planted in cotton and soybeans. Results strongly suggest that cotton production was the primary source of contamination. Actual routes of movement have not been clearly defined but aerial transport seems most probable.

Introduction

In February 1970 the Plant Protection Division, Agricultural Research Service, U.S. Department of Agriculture, initiated a study to determine the magnitude and source of pesticide residues in commercially grown catfish. The study was undertaken to investigate reports of illegal residues of DDT, endrin, and dieldrin in commercially raised catfish of the Mississippi delta, which is the major catfish-growing area of the United States. Analyses for mercury were included for scientific interest.

Although little information is available on pesticide residues in cultured catfish, it is generally known that fish can concentrate chlorinated hydrocarbon pesticides. Bevenue et al. (*1*) reported that chlorinated pesticides can be concentrated to 33,000 and 36,000 times the level found in the water by carnivorous and detrital fish, respectively. Morris and Johnson (*2*) studied the dieldrin level of fish in Iowa streams and found that catfish contained higher pesticide levels than other rough fish and much higher concentrations than game fish. A study of wild catfish in Nebraska revealed the frequent presence of DDTR (DDT + DDE + TDE) and dieldrin (*3*).

Channel catfish have been included regularly as a preferred species for sampling in the National Pesticides Monitoring Program for fish because they are near the top of the food chain (*4*). The two monitoring sites located in the commercial fish-raising area of Arkansas consistently reported endrin residues during the spring and fall of 1967 and 1968 (*5*). DDT residue levels in fish from these two areas are among the highest detected in the Mississippi River System (*6*).

Sampling Procedures

Sampling was conducted in Arkansas and Mississippi because those States encompass the most intensive catfish farming area in the United States. Fifty catfish farms were selected on a probability basis: i.e., each farm had an equal chance of being selected. Approximately 1 farm in 12 was examined. At each farm, fish, source water, pond water, and sediment were sampled from one pond; a feed sample was also collected. Sample collection commenced in March 1970 and was completed by the end of April.

Catfish samples were composed of two or three fish, each about 2 years old and weighing 0.5-0.7 kg. As

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specified in the U.S. Department of Health, Education, and Welfare Food and Drug Administration regulatory methodology, only edible fish flesh was examined for pesticide residues.

One gallon of source water and a composite gallon sample of pond water collected from 5 to 10 different pond locations were taken from each farm.

One composite sediment sample was collected from each pond with a weighted dredge. At least five drag subsamples were taken within 10 feet of shore; another five drags were taken farther from shore.

A sample of catfish feed was collected: when possible, from different feedbags or lots.

Analytical Methods

SEDIMENT

After decanting and discarding excess water, the remaining portion was mixed for 5 minutes in a paint shaker and a 300-g sediment sample was taken. The sample was extracted with 600 ml 3:1 hexane:isopropanol by concentric rotation for 4 hours. Alcohol was removed by three water washes and the hexane extract was dried through anhydrous sodium sulfate. It was then ready for gas-liquid chromatographic (GLC) analysis. A separate portion of sediment was dried at 120°C for 24 hours to obtain a moisture content value. Analytical data on sediment samples were calculated on a dry-weight basis.

WATER

The gallon water sample was shaken before removal of a 500-g subsample. The sample contained some suspended matter and was not filtered before extraction.

The 500-ml sample was extracted three times with 60 ml methylene chloride by shaking in a 1,000-ml separatory funnel. The three extracts of about 180 ml were combined and concentrated to about 5 ml, 100 ml hexane was added, and the sample was concentrated again to 5 ml. All concentrations were performed under a three-ball Snyder column except the final adjustment to 2.5 ml which was performed in a centrifuge tube with a gentle stream of air. At this point the sample extract was ready for analysis.

TISSUE, ALGAE, AND FEED SAMPLES

Feed samples were received in 1-gallon and ½-gallon cans and thoroughly mixed to give a representative sample. Catfish were beheaded, skinned, and eviscerated and the meat and bone were thoroughly macerated in a Hobart food grinder.

A 20-g sample was mixed with 100 ml isopropanol for 2-3 minutes in a Waring blender. Three hundred ml hexane was added and the sample was rotated concentrically for 2 hours. An aliquot representing 15 g was taken, the isopropanol was removed by two water washes, and the hexane was extract-dried through sodium sulfate.

Algae and feed were processed in the same manner as tissue except that 100-g samples of feed were used.

Partitioning of Samples—An aliquot of 15 g was partitioned as follows: the 50-ml hexane sample extract was shaken with 100 ml acetonitrile in a 500-ml separatory funnel, the bottom acetonitrile layer was saved, and the hexane layer was discarded. This step was carried out three times and the acetonitrile layers were combined. The combined acetonitrile extracts were backwashed with 25 ml acetonitrile-saturated hexane and the hexane layer was discarded. The acetonitrile sample extract was concentrated to approximately 10 ml under a three-ball Snyder column and 100 ml hexane was added. The latter two operations were repeated twice and the sample was essentially in hexane. The hexane extract was adjusted to appropriate volume and held at low temperature for subsquent florisil column cleanup and fractionation.

Cleanup and Fractionation—A chromatographic column consisting of a 125-ml flask reservoir attached to an 11-by-500-ml glass tube with a teflon stopcock and a removable glass tip was prepared by placing a small pad of hexane-washed glass wool in the bottom of the column and adding anhydrous granular sodium sulfate to the 1-inch level. Eighteen g 60-120 mesh florisil was poured into the column and evenly packed by tapping the column with a light mallet.

The column was prewashed with 100 ml nanograde hexane and the sample extract representing 5 g of the original sample was quantitatively added to the column when the level of the hexane prewash had reached the top of the upper layer of Na_2SO_4. When the sample extract level reached the top of the column, 100 ml 5 percent methylene chloride in hexane was added and a 250-ml flask marked Fraction 1 was placed under the column. When the liquid level again drained to the top of the column, 100 ml nanograde methylene chloride was added to the reservoir and the original flask was replaced by a second, marked Fraction 2. One ml 0.01 percent Nujol in hexane was added to each elution.

Each elution was concentrated to approximately 5 ml under a Snyder column. One hundred ml hexane was added to each elution and the fractions were again concentrated to approximately 5 ml. Each elution was quantitatively transferred to a 15-ml centrifuge tube and placed in a 40°C water bath. A gentle stream of air was directed into the tubes and the sample volume was reduced to 2.5 ml. Fractions were injected separately onto a gas-liquid chromatograph.

Gas-Liquid Chromatographic Analysis—At least two columns were used for each sample; a third column was also used when necessary. Operating parameters varied for the three columns:

Column 1. 4.8 percent OV-17/6.2 percent QF-1 on Gas-Chrom Q

Temperatures:		
	Injector	250° C
	Oven	200° C
	Detector	210° C

Column 2. 3 percent DC-200 on Gas-Chrom Q

Temperatures:		
	Injector	245° C
	Oven	175° C
	Detector	205° C

Column 3. 9 percent QF-1 on Gas-Chrom Q

Temperatures:		
	Injector	230° to 245° C
	Oven	70° C
	Detector	200° to 205° C

Carrier gas was 5 percent methane in argon or prepurified nitrogen at 80-100 ml/min.

Recoveries were performed for each type of sample. Recoveries were consistent with values from the same type of samples in previous work completed in this laboratory.

Chlorinated pesticides used for recovery studies were heptachlor, heptachlor epoxide, gamma chlordane, *o,p'*-DDE, *p,p'*-DDE, dieldrin, endrin, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-TDE, and aldrin; organophosphorus compounds used were phorate, diazinon, methyl parathion, ethyl parathion, DEF, trithion, and ethion. Recovery was 90 to 100 percent on water and sediment, and 80 percent on tissue, algae, and feed.

Toxaphene was quantitated by comparing the four major peaks with corresponding peaks on a calibrated standard chromatogram whenever possible. In some cases only two peaks could be compared with corresponding peaks from the standard. Chlordane was quantitated by use of the gamma chlordane peak or, if necessary, by comparison with a technical chlordane standard. Quantitations were confirmed by dual-column or triple-column cross-checking and use of p-values (*7*).

Limits of Detection—Minimum detection limts (MDL) in fish, algae, feed, and sediment were 0.01 ppm for all pesticides except mixtures such as chlordane, toxaphene, polychlorinated biphenyls (PCB's), and a few compounds such as EPN or Guthion, which elute later on GLC columns. In these cases, the MDL was 0.03 to 0.10 ppm, depending on the compound and the noise level. Corresponding limits for water were 0.01 or 0.03 to 0.10 ppb.

Mercury Analysis—A sample of mercury weighing approximately 2 g was placed in a 250-ml Erlenmeyer flask and 25 ml concentrated sulfuric acid was added. The sample was heated until the organic matter had dissolved. Organic matter was further oxidized by adding 1.0 ml 30 percent hydrogen peroxide until the sample was colorless. Fifty ml distilled water was added to the sample. After cooling, 5 percent potassium permanganate was added, one drop at a time, until a permanent pink color was attained.

Twenty ml sodium chloride—hydroxylamine sulfate was added and the flask was positioned in the aeration system. Ten ml stannous sulfate was added and the mercury was swept into the cell as elemental mercury. The absorbance reading of the mercury was compared with a standard curve plotted from known amounts of mercury which had been analyzed by the same methods applied to the samples. The MDL was 0.01 ppm. This method of analysis was patterned after that of Hatch and Ott (*8*).

Results

All fish examined showed pesticide residues. Results of the fish analyses (Table 1) indicate that DDTR and mercury were found in all samples; dieldrin, endrin, and toxaphene were present in 89, 76, and 96 percent of the samples, respectively. Chlordane was found once and aldrin existed at low levels in three samples. No other chlorinated hydrocarbon pesticides were detected.

Although most fish samples contained residue levels below the FDA action level or tolerance, a number of samples exceeded the limit. FDA action levels were exceeded by 2 percent of the DDTR samples, 6 percent of the aldrin/dieldrin samples, 4 percent of the endrin samples, and 7 percent of the toxaphene samples. In total, 15 percent of the fish samples exceeded present limits for one or more residues. Toxaphene appears to be the most serious contaminant because it exceeded the action level most frequently and its average concentration was closest to its limit. Average concentration of the four samples exceeding the 5 ppm limit was 13.0 ppm.

Possible sources of pesticide residues in fish would appear limited to source water, sediment, feed, and crops. While it is conceivable that stocked fingerlings were a source of pesticides, no evidence in the study indicates this to have been the case. All the farmers claimed that

TABLE 1. *Pesticide and mercury residues in commercial catfish*

	No. Samples	Percent with Residues	Average Concentration, ppm	FDA Action Limit, ppm	Percent Samples Exceeding Limit	Range Detected Residues, ppm
DDTR	54	100	1.07	5	2	0.09-8.71
Aldrin/Dieldrin	54	89	0.07	0.3	6	0.01-0.87
Endrin	54	76	0.06	0.3	4	0.01-0.41
Toxaphene	54	96	2.1	5	7	0.2-20.7
Mercury	50	100	0.07	0.5	0	0.02-0.35

NOTE: Samples represent edible portions of catfish.

they had not applied any of the contaminating pesticides to the fish ponds.

WATER

Thirty-five samples of pond and source water were examined for chlorinated hydrocarbons. In no instance was any pesticide detected at the 0.01 ppb level. No fish from wells were analyzed for chlorinated hydrocarbons because these compounds are insoluble in water and are not leached to any appreciable extent.

To determine whether lower-level contamination existed, residues in catfish were statistically compared according to the water source in which the fish had been caught. A comparison of log-transformed means of DDT, dieldrin, endrin, and toxaphene residues was made between catfish raised in well water and those raised in surface water. Well-water catfish had significantly higher pesticides (95 percent level) in all cases. These data do not, however, indicate that the pesticide came from wells but, rather, that the pesticide source was associated with wells. Further explanation appears under the crop section of this paper.

During a resampling of some of the fish ponds, several algae samples were collected and analyzed. All five samples showed DDT and toxaphene residues. DDTR and toxaphene levels ranged from 0.10 to 0.97 and from 0.20 to 1.41 ppm, respectively. The absence of chlorinated hydrocarbons from pond water can probably be explained by their low solubility in water. Algae residues, however, indicate that pesticides must have been in the water at some time.

Surface runoff could be a source of pesticide residues but the absence of residues from sediment, which is also transported in runoff, does not support this theory. In addition, commercial fish ponds are generally constructed to avoid surface runoff if clean water is available.

SEDIMENT

Fifty-three sediment samples were examined for chlorinated hydrocarbons. The only chemical found was DDTR, which was present in 18 samples. A correlation analysis of all samples was run to estimate the level of association between DDTR in fish and DDTR in sediment. Results showed a correlation coefficient (r) of 0.287, which indicates a significant deviation from zero at the 95 percent level. If DDTR were derived from the original soil prior to pond formation, the DDT level probably would decrease as the pond aged. No significant difference from zero could be established. Another consideration is that DDTR and toxaphene in fish are closely correlated (99 percent level, $r = 0.60$, $n = 54$), which suggests they are derived from the same source. The absence of toxaphene from sediment samples suggests that sediment is not the source of fish residues for this insecticide.

The absence of pesticide residues from sediment samples could also indicate poor sampling techniques. In the resampling of ponds, DDTR was the only pesticide found. Toxaphene, however, was found in algae which eventually becomes detritus and enters the sediment. Absence of residues could mean that fine surface sediment was not adequately sampled.

FEED

All fish feed from the 43 farms sampled had detectable residues (Table 2). In addition to pesticides shown in Table 2, small amounts of heptachlor, heptachlor epoxide, and Aroclor 1254 were detected in a few samples. A correlation analysis did not indicate a significant asssociation between DDTR, dieldrin, endrin, and toxaphene levels in feed and fish (Table 2). In addition, DDTR and toxaphene residues, which correlate closely in fish, are not correlated in feed ($r = 0.200$). Pesticide residues in feed certainly contribute to the residues found in fish, but the amount appears negligible compared with other sources.

CROPS

To determine whether pesticides used on crops had contributed to contamination of catfish, authors compared the percent of total county acres to which insecticides had been applied (9) with the average fish residue for that county. Resulting correlation coefficients indicate a significant deviation from zero (99 percent level) in

TABLE 2. *Principal pesticide residues in fish feed*

	No. Samples	Percent with Residues	Average Concentration, ppm	Range Detected Residues, ppm	Correlation Coefficient, Fish: Feed
DDTR	43	91	0.120	0.02-0.84	0.005
Dieldrin	43	74	0.007	0.01	0.166
Endrin	43	14	0.002	0.01-0.02	–0.149
Chlordane	43	21	0.016	0.01-0.28	ND
Toxaphene	43	42	0.06	0.1-0.3	0.099
Malathion	43	74	0.051	0.01-0.32	ND

NOTE: $n = 43$, $r = 0.301$ at 95% confidence level; $r = 0.391$ at 99% confidence level.
ND = data insufficient to calculate.

TABLE 3. *Correlations between land use practices and insecticide residues in catfish*

	Acres Receiving Insecticide, %	Acres in Harvested Crops, %	Acres in Cotton, %	Acres in Soybeans, %
		Mississippi[1]		
DDTR				
Corr. Coef.	0.794	0.701	0.830	0.636
95% Conf. Interval	0.551-0.913	0.386-0.870	0.621-0.929	0.281-0.838
DIELDRIN				
Corr. Coef.	0.662	0.587	0.706	0.590
95% Conf. Interval	0.323-0.851	0.208-0.813	0.395-0.872	0.213-0.814
ENDRIN				
Corr. Coef.	0.732	0.690	0.818	0.587
95% Conf. Interval	0.439-0.884	0.369-0.864	0.596-0.923	0.208-0.813
TOXAPHENE				
Corr. Coef.	0.687	0.675	0.767	0.563
95% Conf. Interval	0.363-0.863	0.343-0.857	0.502-0.901	0.174-0.800
		Arkansas[2]		
DDTR: Corr. Coef.	0.295	−0.285	−0.211	−0.238
DIELDRIN: Corr. Coef.	−0.007	0.176	0.143	0.170
ENDRIN: Corr. Coef.	0.547	−0.195	−0.046	−0.171
TOXAPHENE: Corr. Coef.	0.197	−0.019	−0.021	0.024

Mississippi but not in Arkansas (Table 3). Similar results were obtained when the percent of total county acres in harvested crops (*9*) was compared with average fish residues.

The major crops and primary recipients of insecticides in Arkansas and Mississippi are soybeans and cotton (*9*). In the period preceding this study, DDT, endrin, dieldrin, and toxaphene were registered for use on cotton. Of these insecticides, only DDT and toxaphene had been used for more than seed treatment of soybeans. Frequently a combination of DDT and toxaphene had been used several times a year on cotton but usually soybeans had been treated just once every few years to control insect outbreaks (*10*).

Correlations comparing the percent of total county acres in cotton or soybeans in Mississippi and average insecticide residues in fish showed significant deviation from zero at the 99 percent level for both crops (Table 3). Correlation coefficients for cotton and soybeans were not significantly different, but cotton always resulted in a more significant deviation from zero for each insecticide. Correlations in Arkansas were again not significant.

The absence of correlation in Arkansas may be due to two factors. Most Arkansas sites sampled were located in the highly agricultural eastern counties, but in Mississippi, sites were scattered throughout the State. Only in Mississippi, therefore, could agricultural areas be compared with nonagricultural areas. A second reason for the insignificant correlations in Arkansas may be that the northeastern counties have fewer insect problems and generally apply a smaller amount of pesticides than do the southeastern counties.

Because Mississippi data were considered more informative, they were chosen for further examination. Mississippi data were segregated into high-cotton areas (>10 percent of the total county acres in cotton) and low-cotton areas (<10 percent of the total county acres in cotton). Mean pesticide levels in catfish were calculated after logarithmic transformation; both cotton areas were compared using a 95 percent confidence interval about the mean. Since residue data were not normally distributed, log transformation was used to help normalize them.

Results indicate that fish in high-cotton areas have significantly higher concentrations of DDTR, endrin, and toxaphene than they have in low-cotton areas (Table 4). This relationship could account for the high correlation between DDT and toxaphene in fish, for DDT and toxaphene had often been applied together on cotton.

TABLE 4. *Mean pesticide residues and 95 percent confidence intervals for fish from high-cotton versus low-cotton areas, Mississippi*

	Residues, ppm			
	Geometric mean, high-cotton area	Geometric mean, low-cotton area	95% Conf. Interval, high-cotton area	95% Conf. Interval, low-cotton area
DDTR	1.48	0.34	2.40 -0.91	0.53 -0.22
Dieldrin	0.042	0.014	0.090-0.017	0.024-0.007
Endrin	0.063	0.010	0.122-0.030	0.019-0.005
Toxaphene	2.73	0.42	4.42 -1.68	0.85 -0.21

High pesticide levels found in fish grown in well water can also be explained by the association between wells and high-cotton areas: 16 of the 19 farms in Mississippi which use wells as the sole water source are located in high-cotton counties. Residues in sediment were also related to high-cotton counties. Of 12 sediment samples with pesticide residues, 11 were located in such counties.

Pesticide residues in catfish are closely correlated with crops and pesticide use. Considering that larger amounts of pesticides are applied to cotton than to any other crop in this area of the South, this study strongly suggests that cotton is the primary source of contamination in fish ponds. Data indicate that neither source water nor surface runoff appear to be the mechanism of pesticide transport. These data and the general absence of pesticide residues in sediments indicate that aerial transport of pesticides may be the major route of catfish contamination.

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Residues of Methoxychlor and Other Chlorinated Hydrocarbons in Water, Sand, and Selected Fauna Following Injections of Methoxychlor Black Fly Larvicide into the Saskatchewan River, 1972[1]

F. J. H. Fredeen, J. G. Saha, and M. H. Balba

ABSTRACT

In May 1972, 0.309 ppm methoxychlor black fly larvicide was applied in a single test on the North Saskatchewan River. Eight to nine days later residues of 0.05-0.10 ppm methoxychlor occurred in sand 21-22 km downstream from the point of injection. Methoxychlor was not detected in water, insect larvae, shellfish, or muscle tissues of three fish species on the same sampling date. Perhaps because of relatively high oil content in goldeye fish, methoxychlor residues in muscle tissues were 1.0-1.5 ppm in 8 percent of those sampled, 0.21-0.99 in 21 percent, and 0.02-0.20 in 37 percent. In 34 percent of the goldeye fish no residues were detected. Goldeye and other fish collected before or 17 weeks after this injection did not contain detectable levels of methoxychlor. River water in two samples of the injected slug of water collected 6.5 km downstream from the point of injection contained 0.14 and 0.16 ppm methoxychlor. The suspended solids filtered from these samples contained 40 and 47 percent of this methoxychlor (437 and 892 ppm, respectively). Thus methoxychlor may act selectively against filter-feeding species, especially black fly larvae.

Introduction

DDT black fly larvicide was injected once or twice into one or both branches of the Saskatchewan River during most years from 1948 through 1967. By 1968 residues in muscle tissues of fish from the river included up to 0.05 ppm DDT, 0.05 ppm DDD, and 0.06 ppm DDE (*1*).

Methoxychlor black fly larvicide was injected experimentally on 11 occasions into the north and south branches of the river from 1968 through 1972 (*2*). At the conclusion of these tests, and specifically in conjunction with a single test on the North Saskatchewan River in May 1972, samples of water, riverbed sands, clams, insect larvae, and fish were analyzed for methoxychlor residues. It is the single test in May 1972 from which most of the specific data in this paper have been compiled.

Tests with single 15-minute injections of methoxychlor as a black fly larvicide commenced in the South Saskatchewan River in 1968 and in the North Saskatchewan River in 1969. The total number of 15-minute injections of methoxychlor at each of four sites is shown in Figure 1. A commercial 24 percent emulsifiable concentrate was used in seven of the eight experimental injections into the South Saskatchewan River and in all six 15-minute injections into the North Saskatchewan River; a commercial 50 percent wettable powder was used in one 1968 application in the South Saskatchewan River. A total of 285 kg technical methoxychlor was used in the eight injections into the South Saskatchewan; 450 kg was applied in the six injections into the North Saskatchewan. These were the only potential sources of methoxychlor residues in either branch of the Saskatchewan River up to and including May 23, 1972.

That day marked the beginning of the study reported here, a study designed specifically to determine whether methoxychlor residues existed before or after a single 15-minute injection of 0.309 ppm methoxychlor into the North Saskatchewan River at Cecil Ferry (Fig. 1) on May 23. The injection period at Cecil Ferry lasted from 2:37 to 2:52 p.m. The injected mass of water passed the Cecil Rapids site about 4:40 to 5:15 p.m., as indicated by the solvent odor and by drogues that

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had been released at the Cecil Ferry site at the leading and trailing edges of the treated mass of water. The treated water is assumed to have passed the Lacolle Falls site during the night of May 23-24. Figure 1 shows all three sites where samples were collected for analyses of residues. Also on May 23, 0.186 ppm methoxychlor was injected for 15 minutes into the South Saskatchewan River from Birch Hills Ferry. Total injected amounts of technical methoxychlor were 65.0 and 32.7 kg, respectively.

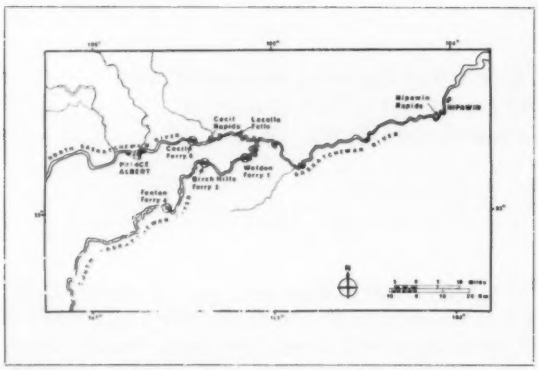

FIGURE 1. *North and South Saskatchewan Rivers, central Saskatchewan, showing injection sites and numbers of methoxychlor black fly larvicide injections, 1968-72*

Prior to May 23, 1972, methoxychlor had last been injected into the river May 21 and June 4, 1971, when two 15-minute injections of 0.143 and 0.301 ppm were made from the Birch Hills Ferry and two 15-minute injections of 0.299 and 0.301 ppm were made from Cecil Ferry.

Sampling

Samples for residue analyses were collected only from the North Saskatchewan River, either from the Cecil Ferry crossing, site of the methoxychlor injection; from Cecil Rapids, 6.5 km downstream from Cecil Ferry; or from Lacolle Falls, 21-22 km downstream from Cecil Ferry (Fig. 1). Average width of the river was about 250 m. Its volume discharges were 236 m^3/second on May 23, about 340 m^3/second on June 1, and about 140 m^3/second on September 19. The riverbed consisted of gravel and rocks interspersed with occasional beds of sand. There were numerous rapids including Lacolle Falls in this section of the river, all navigable by canoe.

Water samples were collected only at midriver sites, either the Cecil Ferry crossing or Cecil Rapids (Table 1); samples were taken before, during, and after passage of the injected water. These samples were collected by hand in Teflon-coated jars which were opened and filled beneath the water surface.

Sand was collected beneath about 60 cm flowing water several meters from both river margins near Lacolle Falls. A hand shovel with 5-cm sides was guided along the riverbed to collect only the uppermost layer of sand to a depth of 0.5 cm. Mussels ranging from about 0.2 to 0.6 cm in diameter were washed out of sand collected from under 30-60 cm water along the north side of the North Saskatchewan River at

TABLE 1. *Methoxychlor residues in samples of water and sand collected from North Saskatchewan River, May-June—1972*

Date Collected	Location	Material Collected	Methoxychlor Content, ppm
		River Water	
May 20: 2 samples	Cecil Ferry	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
May 23: prior to arrival of treated water	Cecil Rapids	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
May 23: 15 min after arrival of leading edge of treated water	Cecil Rapids	Whole water	0.160
		Suspended solids	892.0
		Filtrate	0.085
May 23: 30 min after arrival of leading edge of treated water	Cecil Rapids	Whole water	0.140
		Suspended solids	437.0
		Filtrate	0.084
May 30	Cecil Rapids	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
June 1	Cecil Rapids	Whole water	ND
		Suspended solids	ND
		Filtrate	ND
		Sand	
May 16	Lacolle Falls, N. side	NA	ND
May 16	Lacolle Falls, S. side	NA	ND
June 1	Lacolle Falls, N. side	NA	0.10
June 1	Lacolle Falls, S. side	NA	0.05

NOTE: ND = not detected (<0.01 ppm methoxychlor).
NA = not applicable.

Lacolle Falls. Odonata larvae about 1.5 cm long were also extracted from the sand along with the mussels. Trichoptera larvae about 1.0 cm long were collected from submerged rocks at midriver sites near Lacolle Falls. About 100 small mussels, 100 Odonata larvae, and 30 Trichoptera larvae were collected on each sampling date. Black fly larvae were not available for this study. A nylon net with mesh openings of less than 0.1 mm was used to collect insects drifting in water at Cecil Rapids before and during passage of methoxychlor-injected water. A seine was used to collect fish at Lacolle Falls on May 16 but overnight gill net sets were used on May 17 and 31, June 1, and September 19.

All samples of sand, mussels, insect larvae, and fish were wrapped immediately in aluminum foil and frozen in solid CO_2. They were stored at −18° C until analysis.

Analytical Procedures

All solvents were pesticide analysis grade and were redistilled in glass. Water samples were analyzed within 24 hours of collection. Two-liter aliquots of thoroughly mixed water samples were filtered under suction to remove suspended solids. The filtrate was extracted with 200 ml hexane three times. The combined hexane extract was dried over anhydrous sodium sulfate, concentrated to a suitable volume, and analyzed by electron-capture/gas-liquid chromatography (EC/GLC).

Suspended solids were collected on filter paper, air dried, and weighed. Samples weighing about 0.2 g each were extracted by shaking for 1 hour with 25 ml 4:1 hexane:acetone mixture and filtered. Residues were reextracted twice with the same amounts of solvent mixture. The combined extract was dried over anhydrous sodium sulfate and concentrated to about 10 ml. The concentrated extract was chromatographed on a 20-g florisil column containing 3 percent water and eluted with 200 ml 6 percent diethyl ether in petroleum ether, followed by 200 ml 16 percent diethyl ether in petroleum ether. Combined eluents were concentrated to a suitable volume and analyzed by GLC.

All fish specimens were filleted and only edible muscle tissues without any skin were analyzed for pesticide residues. Fish specimens of the same species and similar sizes were first analyzed as composite samples. For this purpose 4- or 5-g muscles from 4 or 5 fish were pooled into 20-g samples; pesticide residue levels were determined by the method described previously by Fredeen et al. (*1*). If any pooled samples showed residues of methoxychlor, all fish specimens representing the composite were then analyzed separately by the same method.

Mussels, drift net collections, and insect larvae samples were also analyzed by Fredeen's method although they were extracted with 5 ml acetonitrile for each gram of sample.

Riverbottom material which consisted mostly of sand was partly air-dried and thoroughly mixed. Twenty-g aliquot samples were extracted with 1:1 hexane:acetone by the method described earlier by Saha (*3*). Extracts were cleaned and analyzed as described by Fredeen et al. (*1*).

GAS CHROMATOGRAPHY

An Aerograph Hi-Fy gas chromatograph, Model 600D, was used for quantitative analysis. Operating conditions were:

Column:	Aluminum, 5 ft by ⅛ in. ID, packed with 4 percent SE-30 and 6 percent QF-1 on 80-100 mesh chromosorb W.
Detectors:	Electron-capture, with tritium ionizing source.
Temperatures:	Column 185° C. Injector 200° C. Detector 200° C.
Carrier gas:	Oxygen-free nitrogen.
Flow rate:	40 ml/min
Electrometer:	Range 1 Sensitivity 4

Under these conditions retention time for aldrin was 3.0 minutes. Retention times for other organochlorine insecticides relative to aldrin were: heptachlor, 0.94; heptachlor epoxide, 1.81; *p,p'*-DDE, 2.47; dieldrin, 2.81; *p,p'*-DDD, 3.25; *p,p'*-DDT, 3.78; and *p,p'*-methoxychlor, 7.25.

All samples were analyzed for the above-mentioned organochlorine insecticides. Percent recoveries obtained when these chemicals were added at 0.10 and 0.25 ppm to 20-g samples of fish, extracted, and analyzed as above were: heptachlor, 78-92 percent; aldrin, 68-82 percent; heptachlor epoxide, 87-101 percent; *p,p'*-DDE, 68-85 percent; dieldrin, 84-102 percent; *p,p'*-DDD, 71-87 percent; *p,p'*-DDT, 86-98 percent; and *p,p'*-methoxychlor, 86-108 percent. The lower limit of detection was 0.01 ppm. Data reported below are not corrected for percent recovery. Any sample showing more than 0.1 ppm of any of the above organochlorine insecticides was also analyzed by thin-layer chromatography (TLC) according to the method of Kovacs (*4*).

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Presence of methoxychlor in excess of 0.2 ppm in goldeyes was confirmed by gas-liquid chromatography/mass spectrometry (GLC/MS). A Finnigan Model 3000 quadrupole mass spectrometer, connected to a Varian Aerograph Model 1400 gas chromatograph by means of an all-glass single-stage jet separator, was used. A 5-ft-by-⅛-in.-ID glass column packed with 3 percent OV-1 on 60- to 80-mesh Gas Chrom Q was used for GLC separation. Column temperature was 210° C and helium flow rate was 15 ml/min. Mass spectra were recorded at 70 eV electron energy and sweep time of 10 seconds. Mass spectrum could be obtained when

2.5 μg reference methoxychlor was injected into the gas chromatograph.

About 100 g fish containing more than 0.2 ppm methoxychlor as shown by gas chromatographic analysis was extracted and cleaned by the method described above. Cleanup extract was concentrated to about 100 μl, and 5- to 25-μl samples were injected into the GLC/MS system. Recorded spectra were compared with those of reference methoxychlor. Presence of methoxychlor in water was also confirmed by GLC/MS.

Results and Discussion

RESIDUES IN RIVER WATER

Methoxychlor was detected only in river water collected directly from treated water that passed the sampling point in Cecil Rapids (Table 1). No residues were detected in water collected either before or 1 week after the passage of the injected water.

The leading edge of the treated water, indicated by drogues and the odor of the concentrate, required 2 hours to travel from the injection point to Cecil Rapids. Water collected at Cecil Rapids 15 minutes after arrival of the leading edge contained 0.16 ppm methoxychlor; water collected another 15 minutes later contained 0.14 ppm. The injected water thus required at least 30 minutes to pass this site, indicating a doubling of its volume during its travel 6.5 km downstream from the point of injection. At the same time methoxychlor concentration was reduced by 50 percent from 0.309 to 0.14-0.16 ppm. This indicates that the treated mass of water became progressively more diluted, simultaneously expanding in volume as it moved downstream to the point where sand and faunal samples were collected.

The two water samples collected from Cecil Rapids 15 and 30 minutes after arrival of the leading edge contained about 85 and 125 ppm suspended solids, respectively. More than half the suspended solids consisted of very fine sand with particle diameters of 0.05-0.1 mm. The remainder consisted of silt and clay particles and a small proportion of organic material. Suspended solids in these two water samples contained 892 and 437 ppm methoxychlor, respectively; filtrates contained 0.085 and 0.084 ppm, respectively. Thus the suspended solids contained about 47 and 40 percent, respectively, of the total methoxychlor extracted from the two water samples.

Merna et al. (*5*) noted that when methoxychlor was added to lake water containing plankton, most of the compound eventually became associated with the particulate fraction. Fredeen et al. (*6*) showed that suspended solids filtered from the South Saskatchewan River 68 miles downstream from the application point of DDT black fly larvicide contained 0.24 to 2.26 ppm DDT. The DDT absorbed onto these suspended particles was believed able to act as a selective poison against filter-feeding insect larvae, including *Simulium arcticum*, the target species. Because methoxychlor is also readily adsorbed onto suspended particles, it could also be more toxic to filter-feeding insect larvae in the Saskatchewan River than to nonfilter feeders. Methoxychlor applied to the river did prove much more destructive to *Simulium* larvae than to Trichoptera larvae. However, nonfilter feeders such as Plecoptera larvae were also severely affected (*2*).

RESIDUES IN SAND

Nine days after methoxychlor injection, sand and silt collected from the riverbed 21-22 km downstream from the point of injection also contained methoxychlor (Table 1). Sand from the north side of the river contained 0.1 ppm methoxychlor; sand from the south side contained 0.05 ppm. The difference in concentrations may have been caused by differences in sampling depths or by the varied proportions of sand and silt deposited on each side. Unfortunately no information is available on these characteristics. No residues were detected in samples collected before the May 23 injection. The limited number of samples did not enable authors to calculate the rate of methoxychlor loss from the injected water. The fact that no methoxychlor was detected in any pretreatment samples proves that residues did not persist from treatments in 1971 or earlier.

RESIDUES IN MUSSELS

No methoxychlor residues were detected in mussels collected from riverbed sand 21-22 km downstream from the point of injection (Table 2). In 1968 Bedford et al. (*7*) showed that two species of freshwater mussels in the Red Cedar River in Michigan contained DDT and its metabolites, plus aldrin and methoxychlor. Concentrations of methoxychlor in these mussels range from nondetectable to 0.22 ppm. At the time of their study in the mid 1960s, methoxychlor, DDT, and malathion were used annually in the vicinity of the Red Cedar River to control elm bark beetles and mosquitoes. Thus it is presumed that mussels in the Red Cedar River were continuously exposed to these chemicals for long periods of time. Mussels collected from the river had been exposed to about 0.15 ppm methoxychlor in the water for only an hour or so; they were exposed to about 0.1 ppm in sand for about 8 days. Kapoor et al. (*8*) showed that in an aquarium ecosystem, snails exposed to methoxychlor for about 13 days accumulated relatively large amounts of the compound, whereas the methoxychlor content of fish remained in dynamic equilibrium with levels in their environment.

RESIDUES IN INSECT LARVAE

No methoxychlor residues were detected in the larvae of Odonata or Trichoptera collected alive from the riverbed either 6-7 days before or 8-9 days after treatment

of the river with methoxychlor on May 23, 1972 (Table 2). However, larvae of these and other families of aquatic insects, including Plecoptera, Ephemeroptera, and Diptera, that were disabled by methoxychlor and collected with a net during the actual passage of injected water, contained an average of 17.5 ppm methoxychlor. Presumably fish that ate insects disabled or killed by such a treatment would be exposed to relatively high concentrations.

RESIDUES IN PRETREATMENT FISH

No methoxychlor was found in any pretreatment fish except goldeye (Table 3), although other chlorinated hydrocarbons were detected. DDT and related compounds were detected in 60 percent of the goldeye and 64 percent of the suckers; heptachlor and heptachlor epoxide were detected in 60 percent of the goldeye. Levels of these chemicals indicated by GLC were less than 0.1 ppm, too low to be confirmed by TLC. No residues of chlorinated hydrocarbons were detected in pickerel, sauger, or northern pike.

RESIDUES IN POSTTREATMENT FISH

Methoxychlor was detected in the muscle tissues of 66 percent of the goldeye collected 8-9 days after the 15-minute injection of 0.309 ppm methoxychlor about 21-22 km upstream from the fish-collecting site. In 37 percent of the goldeye, methoxychlor concentrations in muscle tissues ranged from 0.02 to 0.20 ppm; in 21 percent, concentrations ranged from 0.21 to 0.99 ppm; in 8 percent of this species, they ranged from 1.0 to 1.5 ppm; and in 34 percent, there were no detectable residues. Presence of methoxychlor could be confirmed in 47 percent of the goldeye by TLC, and in 21 percent by mass spectrometry. Mass spectra in these samples were the same as those of the reference methoxychlor. No methoxychlor was detected in any other species of fish collected 8-9 days after treatment.

As in pretreatment samples, other chlorinated hydrocarbons were also detected in these fish. Residues were less than 0.1 ppm except in the goldeye where levels of up to 0.16 ppm aldrin and dieldrin and up to 0.51 ppm DDT and related compounds were detected.

TABLE 2. *Methoxychlor residues in clams and insect larvae collected from North Saskatchewan River, May-June—1972*

Date Collected	Location	Specimen	Methoxychlor Content, ppm
May 16	Lacolle Falls, N. side	About 100 small mussels	ND
May 17	Lacolle Falls, N. side	About 100 small mussels	ND
May 31	Lacolle Falls, N. side	About 100 small mussels	ND
May 16	Lacolle Falls, N. side	About 100 Odonata larvae	ND
May 17	Lacolle Falls, N. side	About 100 Odonata larvae	ND
May 31	Lacolle Falls, N. side	About 100 Odonata larvae	ND
June 1	Lacolle Falls, N. side	About 30 Trichoptera larvae	ND
June 1	Lacolle Falls, S. side	About 30 Trichoptera larvae	ND
May 23: before treatment	Cecil Rapids, midriver	About 50 insect larvae	ND
May 23: during treatment	Cecil Rapids, midriver	About 1,000 disabled insect larvae	17.5

NOTE: ND = not detected (< 0.01 ppm methoxychlor).

TABLE 3. *Residues of chlorinated hydrocarbon insecticides in muscle tissues of fish collected from North Saskatchewan River before and after methoxychlor injection, May 1972*

Common Name	No. Fish Analyzed	Heptachlor and Heptachlor Epoxide		Aldrin and Dieldrin		DDT, DDE, and DDD		Methoxychlor	
		Percent of Positive Samples	Range, ppm	Percent of Positive Samples	Range, ppm	Percent of Positive Samples	Range, ppm	Percent of Positive Samples	Range, ppm
May 16 and 17, 1972									
Goldeye	25	60	0.02-0.05	40	0.01-0.08	60	0.01-0.04	0	ND
Sucker	14	0	ND	0	ND	64	0.01-0.04	0	ND
Pickerel and Sauger	12	0	ND	0	ND	0	ND	0	ND
Northern Pike	8	0	ND	0	ND	0	ND	0	ND
May 31 and June 1, 1972									
Goldeye	38	39	0.01-0.05	29	0.01-0.16	39	0.03-0.51	66	0.02-1.5
Sucker	3	0	ND	66	0.02-0.03	33	0.03	0	ND
Pickerel and Sauger	7	100	0.02	14	0.01	0	ND	0	ND
Northern Pike	19	26	0.02	0	ND	47	0.01	0	ND
September 19, 1972									
Goldeye	6	0	ND	0	ND	0	ND	0	ND
Sucker	9	0	ND	0	ND	0	ND	0	ND
Pickerel and Sauger	6	0	ND	0	ND	0	ND	0	ND
Northern Pike	2	0	ND	0	ND	0	ND	0	ND

NOTE: ND = not detected (< 0.01 ppm).

RESIDUES IN FISH: 17 WEEKS POSTTREATMENT

Methoxychlor could not be detected in the muscle tissues of any species of fish including goldeye collected from this same site September 19, 1972.

RESIDUES IN FISH: GENERAL CONSIDERATIONS

Considering their similar trophic levels, it was surprising that goldeye and other fish species had such disparate residues of methoxychlor 8-9 days after injection. The authors had expected relatively low concentrations of residues in goldeye, which graze mainly on insect colonies attached to rock surfaces, and relatively high concentrations in fish-feeding species such as pickerel, sauger, and northern pike, and in suckers, which are bottom-feeders and could have engorged on masses of immobilized larvae.

The relatively higher concentrations of methoxychlor and other chlorinated hydrocarbons in goldeye muscle tissues may be explained by the relatively high oil content of their muscle tissues. Schmidt (*9*) reported that muscle tissue of one sample of six goldeye contained 6.57 percent fat; three samples of pickerel including 18 fish contained 2.84-3.34 percent fat; three samples of suckers including 18 fish contained 3.01-3.68 percent fat; and two samples of pike including 11 fish contained 1.40-1.86 percent fat.

Let us assume that methoxychlor extracted from muscle tissues of goldeye fish in this study originated only from the fat fraction, and that these muscle tissues contained 6.57 percent fat. Then, in 37 percent of the goldeyes, methoxychlor concentrations in fat fractions could have ranged from 0.3 to 3.0 ppm; in 21 percent, from 3.2 to 15.0 ppm; in 8 percent, from 15.2 to 22.7 ppm: and in 34 percent, concentrations would be less than 0.3 ppm. These levels do not demand government action, both because of the residues' ephemeral nature, presumably due to brief exposure in the river and rapid elimination from the fish, and because fish fat, unlike the fat of livestock, is not used separately as a food item for humans. In the case of livestock fat, concentrations of methoxychlor above 3 ppm rate government intervention.

Conclusions

Results indicate that a single 15-minute injection of 0.309 ppm methoxychlor into the Saskatchewan River contaminated water and biota for a short time at least as far as 22 km downstream. However, no detectable residues of methoxychlor remained from similar treatments of previous years.

Like other organochlorine insecticides, notably DDT, methoxychlor was readily adsorbed onto suspended particles in water resulting in very high residue concentrations.

No residues were detected in insect larvae or mussels that inhabited the riverbed. Of all fish species examined here, only goldeye showed tendencies to accumulate methoxychlor. Concentrations which did accumulate in the edible flesh of about 80 percent of the goldeye were smaller than the concentration injected into the water 8-9 days earlier. The absence of methoxychlor residues in other species of fish may have been related to the relatively low oil content of their muscle tissues, as well as their ability to rapidly eliminate it from their systems as indicated by Kapoor et al. for *Gambusia affinis* fish (*8*). No methoxychlor residues were detected in goldeye or other fish 17 weeks after the experimental treatment.

Acknowledgment

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Organochlorine Residues in Starlings, 1972

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ABSTRACT

During the fall of 1972 starlings were collected from 130 sites in conjunction with the National Pesticide Monitoring Program. They were analyzed for DDT and its metabolites, dieldrin, heptachlor epoxide, benzene hexachloride, polychlorinated biphenyls and, for the first time in the series, oxychlordane and HCB. Mean DDT and dieldrin residue levels have declined significantly since 1967 and a regression analysis suggests that levels of DDT and its metabolites should fall below a mean of 0.1 ppm for the 1974 starling collection.

Introduction

As part of the National Pesticide Monitoring Program, a nationwide sample of starlings is collected and analyzed biennially to help measure environmental levels of persistent organochlorine compounds. Data for residues of these contaminants were first derived from analyses of three collections taken in 1967 and 1968 and reported by Martin in 1969 (*1*). The rationale for selecting starlings as a subject species appeared in that pilot study: they are a terrestrial avian species found year-round throughout most of the contiguous United States; they are generally regarded as expendable; and their omnivorous feeding habits can be expected to reflect pesticide intake from insects, fruits, grain, and miscellaneous other foods. Collections from fall 1970 were reported by Martin and Nickerson in 1972 (*2*). The present paper presents data from the fall 1972 collection and compares portions of the data to those obtained in previous collections. Using these data, authors can examine some trends with greater confidence than in past studies and make tentative estimates for residue levels of DDT and dieldrin in future collections. Focus of the estimates will be national rather than regional, leaving the problem of substantial geographical variation for the future.

Sampling

As described in previous publications, the sampled area is composed of 40 blocks of 5° latitude and longitude, ranging from 24° to 49° latitude and 64° to 124° longitude (*1,2*). One to four starling sampling sites were randomly selected from each block. The same sites have been used for all collections. Figure 1 shows the location of all sampling sites and Table 1 lists locations successfully sampled during the November-December 1972 collection. Each sample location is identified by a row number, a column letter, and a site number: e.g., the site near Tacoma, Wash., is designated 1-A-1. In 1972, collections were made at 130 (94 percent) of 139 sampling locations.

In previous years, Texas, a State of high pesticide use, posed a major problem. Thus collection efforts were intensified in 1972 and collections were successful in five of the nine preselected sites. Hopefully sampling in Texas will be improved further by extending the collection period into January when the starlings are in larger flocks.

Most starling samples consisted of a pool of 10 birds which had been trapped or shot. Each pool was wrapped in aluminum foil, placed in polyethylene bags, and frozen for shipment to the laboratory.

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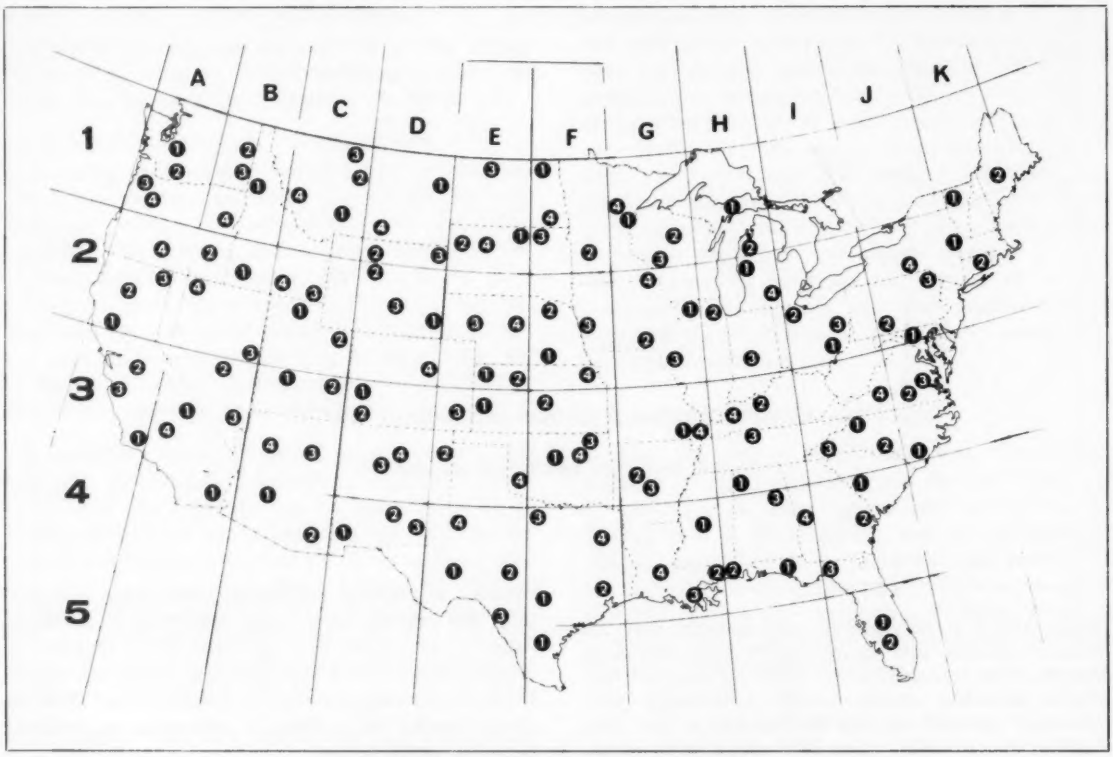

FIGURE 1. *Starling monitoring sites, 1972*

Analytical Methods

Residue analyses were performed as described previously (*1,2*) by WARF Institute, Inc., under contract with the U.S. Department of Interior—Bureau of Sport Fisheries and Wildlife (predecessor of the Fish and Wildlife Service). Technicians prepared the birds by removing their beaks and feet, then skinning their bodies. Each pool was ground in a Hobart food chopper until homogenized. The only major change in methodology involved use of 11 percent OV-17 + QF-1 (mixed phase) on 80/100 Gas-Chrom Q in the second column. Flow rate involved a retention time of 4-5 minutes for heptachlor epoxide. This new procedure separated oxychlordane from heptachlor epoxide, and HCB from BHC.

For the determination of DDE, DDD, DDT, dieldrin, and polychlorinated biphenyls (PCB's), instrument conditions were:

Temperatures:	Column 200° C. Injector 230° C. Detector 240° C.
Column:	4-ft-by-4-mm glass packed with 5 percent DC-200 on 80/100 Gas-Chrom Q.
Carrier Gas:	Nitrogen.
Flow:	Involved retention time of 6-8 minutes for *p,p'*-DDT.

For the determination of HCB, alpha BHC, gamma BHC (lindane), beta BHC, heptachlor epoxide, and oxychlordane, instrument conditions were:

Temperatures:	Column 180° C. Injector 220° C. Detector 235° C.
Column:	4-ft-by-4-mm 11 percent OV-17 + QF-1 (mixed phase) on 80/100 Gas-Chrom Q (available from Applied Science Cat. No. 12970).
Carrier Gas:	Nitrogen.
Flow:	Involved retention time of 4-5 minutes for heptachlor epoxide.

Recovery rates for DDE, DDD, DDT, PCB's, dieldrin, and BHC ranged from 78 to 97 percent. Residue data were not corrected for recovery. Recovery and confirmatory tests were performed internally by the commercial laboratory on a quality control basis. Limits of detection ranged from 0.005 to 0.1 ppm.

TABLE 1. . *Starling sampling sites listed by State and county, 1972*

State	County	Site Number
Alabama	Marion	3-H-1
	Talladega	4-H-3
Arizona	Navajo	3-C-3
	Yavapai	3-C-4
	Maricopa	4-C-1
	Graham	4-C-2
Arkansas	Yell/Pope	3-G-2
	Lonoke/Pulaski	3-G-3
California	Colusa	2-A-1
	Shasta	2-A-2
	Modoc	2-A-3
	Ventura	3-A-1
	Stanislaus	3-A-2
	Monterey	3-A-3
	Inyo	3-B-1
	Kern	3-B-4
	Imperial	4-B-1
Colorado	Weld	2-D-4
	Montrose	3-D-1
	Crowley	3-D-2
Connecticut	New London	2-D-2
Florida	Bay	4-H-1
	Madison	4-I-3
	Polk	5-I-1
	Hardee	5-I-2
Georgia	Pike	4-H-4
	Wayne	4-I-2
Idaho	Nez Perce	1-B-1
	Owyhee	2-B-1
	Franklin	2-C-3
	Minidoka	2-C-4
Illinois	Stephenson	2-G-1
	Adams	2-G-3
	Kane	2-H-2
Indiana	Hendricks	2-H-3
Iowa	Fremont	2-F-3
	Jasper	2-G-2
	Marshall	2-G-4
Kansas	Rawlins	2-E-1
	Phillips	2-E-2
	Kearny	3-E-1
	Nemaha	2-F-4
	Marion	3-F-2
Kentucky	Ohio	3-H-2
	Hopkins	3-H-4
Louisiana	Jefferson	4-G-3
	Rapides	4-G-4
Maine	Penobscot	1-K-2
Maryland	Prince Georges	2-J-1
Michigan	Chippewa	1-H-1
	Grand Traverse	1-H-2
	Kent	2-H-1
	Ingham	2-H-4
Minnesota	Aitkin	1-G-4
Mississippi	Leake	4-G-1
	Harrison	4-G-2
	Jackson	4-H-2
Missouri	Butler	3-G-1
	Bollinger	3-G-4
Montana	Meagher	1-C-1
	Blaine	1-C-2
	Missoula	1-C-4
	Richland	1-D-1
	Yellowstone	1-D-4
Nebraska	Keith	2-E-3
	Brown	2-E-4
	Lancaster	2-F-1
	Clay	2-F-2
Nevada	White Pine	2-B-3
	Humboldt	2-B-4
	Nye	3-B-2
	Clark	3-B-3
New Mexico	Bernalillo	3-D-3
	Torrance	3-D-4
	Luna	4-D-1
	Otero	4-D-2
	Chaves	4-D-3
	Quay	3-E-2
New York	Jefferson	2-J-4
	Rensselaer	2-K-1
North Carolina	Wilkes	3-I-1
	Union	3-I-2
	Macon	3-I-3
	Pender	3-J-1
North Dakota	McLean	1-E-3
	Grand Forks	1-F-1
	Ransom	1-F-4
Ohio	Pickaway	2-I-1
	Wood	2-I-2
	Noble	2-I-3
Oklahoma	Greer	3-E-4
	Canadian	3-F-1
	Nowata	3-F-3
	Okmulgee	3-F-4
Oregon	Yamhill	1-A-3
	Lane	1-A-4
	Klamath	2-A-4
	Baker	1-B-4
	Harney	2-B-2
Pennsylvania	Somerset	2-J-2
	Luzerne	2-J-3
South Carolina	Aiken	4-I-1
South Dakota	Potter	1-E-1
	Butte	1-E-2
	Hughes	1-E-4
	Brown	1-F-3
Tennessee	Davidson	3-H-3
Texas	Kinney	4-E-3
	Cochran	4-E-4
	Comal	4-F-1
	Clay	4-F-3
	San Patricio	5-F-1
Utah	Weber	2-C-1
	Duchesne	2-C-2
	Sevier/Millard	3-C-1
	Grand	3-C-2
Vermont	Addison	1-K-1
Virginia	Amherst	3-I-4
	Prince George	3-J-2
	Caroline	3-J-3
Washington	Pierce	1-A-1
	Yakima	1-A-2
	Spokane	1-B-2
	Whitman	1-B-3
Wisconsin	Clark	1-G-2
	Trempealeau	1-G-3
Wyoming	Big Horn	1-D-2
	Crook	1-D-3
	Goshen	2-D-1
	Washakie	2-D-2

Statistical Procedures

National averages for DDT with its metabolites and dieldrin from all five collections were calculated by two methods (Table 2). The geometric mean provides an appropriate measure of central tendency and should approximate the median value in these skewed distributions (see reference *2*, Table 4). The arithmetic means average 2.2 times higher than the geometric means for DDT and metabolites, and 2.7 times higher for dieldrin. The arithmetic mean is a better measure of environmental load and is the appropriate value to use in determining, for example, how much pesticide a Cooper's hawk would be likely to ingest if it ate 100 starlings. The estimate cannot be precise because of the low probability of encountering starlings with unusually high concentrations of pesticides (Tables 3,4). In calculating the means, values given as <0.015-<0.010 ppm in the pilot study of this series (*1*) were assigned values of 0.005 ppm. For 1972, trace was called 0.002 ppm.

The confidence intervals around the geometric means reflect the nationwide variability in residue levels and are not the most sensitive indicators of differences between the annual means. Residue values of DDT and its metabolites from each station were compared with those of dieldrin for the periods summer-winter 1967-68 versus fall 1968, fall 1968 versus fall 1970, and fall 1970 versus fall 1972. Statistically significant correlation coefficients ranged from 0.59 to 0.70 for DDT and from 0.26 to 0.56 for dieldrin, indicating that a sign test (*3*) for paired values is an appropriate measure of temporal differences, even though the residual variance is high.

Having established that certain differences between years were statistically significant, regression analysis

TABLE 2. *Geometric and arithmetic means of DDT and dieldrin residues in starlings, 1972*

Collecting Period	No. Stations Sampled	Lipids, % Wet Weight	DDT & Metabolites, ppb Wet Weight	Dieldrin, ppb Wet Weight
Summer 1967	116	3.20 (3.01-3.41)	679 (536-861) AM 1755	27 (21-34) AM 82
Winter 1967-68	122	7.42 (6.99-7.87)	830 (670-1028) AM 2019	99 (74-134) AM 240
Fall 1968	122	5.84 (5.47-6.23)	569 (473-685) AM 1135	40 (32-49) AM 84
Fall 1970	125	5.40 (5.00-5.82)	445 (366-539) AM 916	36 (29-46) AM 117
Fall 1972	130	6.24 (5.89-6.61)	442 (420-464) AM 847	35 (28-45) AM 98

NOTE: Values in parentheses represent 95 percent confidence intervals for geometric mean.
AM = Arithmetic mean.

TABLE 3. *Sites with residue levels of DDT and its metabolites greater than 3.0 ppm in baseline, 1970, or 1972 collections*

Site Number	DDT Residues, ppm		
	Baseline Data, 1967-68	1970	1972
3-A-1	1.903	3.660	1.930
3-B-4	4.376	2.837	2.330
2-C-2	9.551	NS	0.640
3-C-2	3.163	NS	0.610
4-C-1	23.902	14.874	0.140
4-D-1	1.930	4.780	1.100
4-D-3	19.680	1.479	3.550
2-E-1	0.199	0.202	4.130
3-E-4	4.948	5.318	0.330
3-G-3	5.950	5.313	8.040
4-G-1	8.128	3.413	4.950
4-G-2	1.580	4.801	0.710
4-G-4	4.220	1.210	11.800
4-H-3	2.347	3.060	3.290
4-H-4	3.510	2.546	0.880
4-I-1	5.483	3.026	5.080
4-I-3	5.668	3.872	1.680

NOTE: NS = No sample collected.

TABLE 4. *Sites with residue levels of dieldrin greater than 0.3 ppm in baseline, 1970, and/or 1972 collections*

Site Number	Dieldrin Residues, ppm		
	Baseline Data, 1967-68	1970	1972
1-A-3	0.528	0.160	0.160
1-A-4	0.492	0.140	0.130
1-B-1	0.115	0.050	1.560
1-B-2	0.237	0.280	0.710
1-B-3	0.587	0.600	0.037
1-B-4	0.418	0.018	0.009
3-E-1	0.102	0.420	0.041
2-G-1	0.280	0.590	0.090
2-G-3	0.657	3.590	0.390
2-G-4	0.032	1.520	0.310
3-G-1	0.403	0.230	0.260
3-G-3	0.317	0.067	0.110
3-G-4	0.207	0.520	0.350
4-G-2	0.970	0.067	0.011
2-H-2	0.208	0.330	0.170
2-H-3	0.056	0.260	0.340
4-H-1	0.135	0.087	0.310
2-I-2	0.193	0.230	0.730
3-I-1	1.385	0.018	0.076
4-I-2	0.027	0.750	0.022
4-I-3	0.055	0.044	1.200
3-J-1	0.333	0.160	0.530

was used to determine the relationship between residue levels and estimates of pesticide usage. The residue values for fall 1967 were estimated by converting the summer and winter values to a lipid basis and interpolating on a logarithmic scale. Mean lipid values from the three fall collections (Table 2) were then used to estimate the wet-weight residue concentrations for the missing collection.

Residue levels of organochlorine compounds from the 130 stations sampled in 1972 are presented in Table 5.

Results and Discussion

DDT AND METABOLITES

Differences between the residue levels in collections from summer 1967 and winter 1967-68 were not statistically significant (Table 2). Levels in the fall 1968 samples, however, were consistently lower than those found in the corresponding averages for the summer/winter samples, suggesting that a significant change in residue levels had occurred within what had been considered the baseline periods (*1*). Pesticide use preceding the four fall periods was assumed to be proportional to U.S. Department of Agriculture values for domestic disappearance (*4*). Residue levels and pesticide use are highly correlated (Fig. 2) and an extrapolation from the data points predicts a mean residue level well below 0.1 ppm for 1974.

Considerable caution should be exercised in projecting estimates far beyond this data base. The high correlation from only four data points could be fortuitous; authors believe use patterns to be more relevant than mere tonnage in determining exposure. Results from 1974 should provide a more reliable fix on the slope.

Sites having DDT and metabolite residues greater than 3.0 ppm in baseline, 1970, and/or 1972 are listed in Table 3. Sites containing the highest DDT and metabolic levels in 1972 (greater than 3.0 ppm) were found in southeastern New Mexico (4-D-3), northwestern Kansas (2-E-1), central Arkansas (3-G-3), central Louisiana (4-D-3), north-central Alabama (4-H-3), and South Carolina (4-I-1).

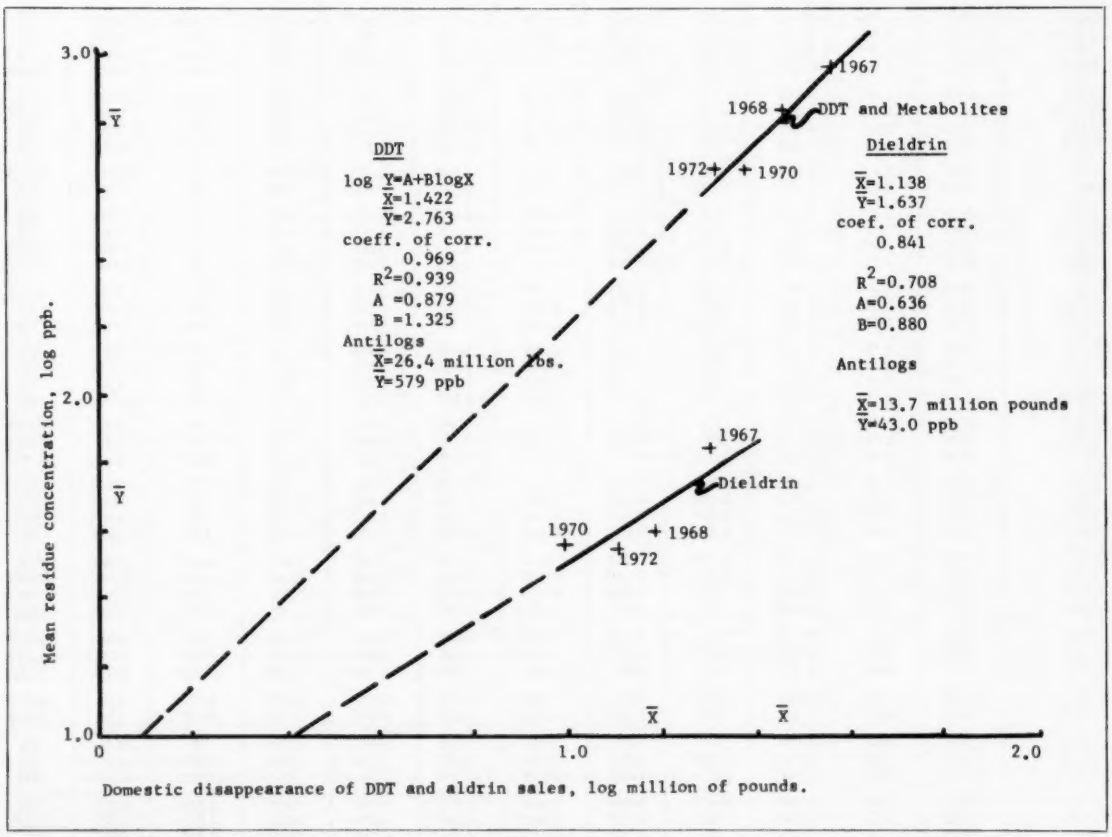

FIGURE 2. *Regressions of pesticide residues in starlings on indices of pesticide use, 1967-68, 1970, 1972*

TABLE 5. *Organochlorine residue levels in starlings, 1972*

Site, No.[1]	Wet Weight, g	Lipid Weight, g	DDE	DDD	DDT	DDT/ Metabolites	PCB's [2]	Dieldrin	Heptachlor Epoxide	Oxychlordane	BHC	HCB
1-A-1	20.03	1.28	0.310	0.017	0.031	0.360	0.360	0.086	0.008	0.007	0.006	0.007
1-A-2	19.97	1.50	1.390	0.006	0.011	1.410	0.063	0.140	0.026	TR	0.036	3.330
1-A-3	20.24	0.83	0.950	0.015	0.017	0.980	0.140	0.160	TR	TR	ND	0.036
1-A-4	20.00	1.19	0.780	0.017	0.019	0.820	0.160	0.130	0.006	TR	TR	0.011
2-A-1	20.16	0.53	0.470	0.008	0.010	0.490	0.074	0.021	TR	TR	0.011	0.011
2-A-2	20.08	0.85	0.630	TR	0.010	0.640	0.100	0.055	0.009	TR	TR	0.014
2-A-3	20.02	1.69	0.077	TR	0.005	0.082	0.056	0.016	TR	TR	0.007	0.011
2-A-4	20.09	1.13	0.490	0.520	0.017	1.030	0.110	0.050	0.013	TR	0.007	0.066
3-A-1	20.10	0.85	1.900	0.014	0.019	1.930	0.170	0.016	0.005	0.008	TR	0.012
3-A-2	20.10	1.06	0.940	0.022	0.053	1.010	0.420	0.037	TR	0.005	TR	TR
3-A-3	20.00	1.32	0.300	0.011	0.019	0.330	0.190	0.019	0.006	0.006	0.007	TR
1-B-1	20.02	1.89	0.660	0.028	0.021	0.710	0.120	1.560	0.009	TR	0.006	2.340
1-B-2	20.03	2.91	0.300	0.014	0.021	0.330	0.170	0.710	0.010	0.007	TR	0.590
1-B-3	20.06	0.95	0.190	TR	0.011	0.200	0.037	0.037	0.210	0.010	0.035	0.550
1-B-4	20.33	1.36	0.150	0.008	0.012	0.170	0.100	0.009	TR	TR	0.010	0.036
2-B-1	20.09	0.98	0.270	0.011	0.029	0.310	0.230	0.060	0.007	TR	0.006	0.057
2-B-2	20.15	1.27	0.170	0.008	0.017	0.200	0.120	0.019	TR	TR	0.009	0.006
2-B-3	20.04	1.96	0.650	0.006	0.014	0.670	0.250	0.046	0.025	ND	0.009	0.007
2-B-4	20.20	1.58	0.240	TR	0.006	0.250	0.099	0.019	0.011	0.006	0.006	0.009
3-B-1	20.02	0.62	2.340	0.009	0.034	2.380	0.370	0.070	0.017	0.017	0.005	0.018
3-B-2	20.29	0.91	0.180	TR	0.006	0.190	0.099	0.039	TR	0.009	0.006	0.005
3-B-3	20.05	1.56	0.620	0.047	0.160	0.830	1.870	0.270	0.053	0.031	0.009	0.037
3-B-4	20.01	1.39	2.310	TR	0.022	2.330	0.140	0.037	TR	0.006	TR	0.024
4-B-1	20.01	0.75	1.440	TR	0.017	1.460	0.190	0.026	TR	TR	TR	0.009
1-C-1	20.54	1.26	0.091	0.009	0.032	0.130	0.370	0.025	0.046	0.030	0.010	0.006
1-C-2	20.05	1.28	0.078	0.016	0.019	0.110	0.210	0.021	0.050	0.009	0.016	0.007
1-C-4	20.48	1.05	0.081	0.013	0.024	0.120	0.290	TR	0.009	ND	0.005	0.009
2-C-1	20.18	1.39	0.350	TR	0.015	0.370	0.150	0.017	0.008	0.006	0.006	TR
2-C-2[3]	20.24	1.13	0.630	TR	0.007	0.640	0.068	TR	0.008	TR	TR	TR
2-C-3	20.11	1.02	0.530	0.006	0.012	0.550	0.120	0.017	0.027	0.009	0.005	TR
2-C-4	20.14	1.66	0.970	0.006	0.012	0.990	0.087	0.028	0.021	0.007	0.006	0.006
3-C-1	20.00	1.66	0.630	TR	0.009	0.640	0.150	0.034	0.011	0.008	0.006	TR
3-C-2[4]	20.16	1.60	0.590	0.006	0.011	0.610	0.200	0.160	0.012	0.007	0.006	0.006
3-C-3	20.02	0.99	0.590	0.005	0.020	0.610	0.250	0.012	TR	TR	TR	TR
3-C-4	19.98	1.01	0.490	TR	0.014	0.500	0.110	0.300	0.007	0.006	0.006	TR
4-C-1	19.99	1.82	0.130	TR	0.009	0.140	0.081	0.021	0.008	TR	0.011	0.025
4-C-2	19.99	0.91	1.490	0.011	0.022	1.520	0.160	0.020	0.006	TR	0.006	TR
1-D-1	20.34	1.39	0.025	TR	TR	0.025	0.037	0.018	0.005	TR	0.006	TR
1-D-2[5]	20.09	1.02	0.077	TR	0.006	0.083	0.100	0.005	0.006	TR	TR	TR
1-D-3[6]	20.02	1.66	0.058	0.011	0.052	0.120	0.750	0.009	0.007	TR	0.006	0.005
1-D-4	20.38	1.85	0.076	TR	0.009	0.085	0.061	0.025	0.007	TR	0.005	0.007
2-D-1	19.95	1.49	0.071	0.008	0.017	0.096	0.250	0.006	0.010	ND	TR	0.005
2-D-2[4]	20.16	0.72	0.050	TR	0.006	0.056	0.099	0.006	0.009	ND	0.007	TR
2-D-4	20.06	1.75	0.220	TR	0.016	0.240	0.190	0.049	0.011	0.011	0.007	TR
3-D-1	20.05	0.92	0.260	TR	0.012	0.270	0.120	0.066	0.013	0.013	TR	TR
3-D-2	20.02	1.34	0.079	TR	0.009	0.088	0.094	0.007	TR	TR	0.009	TR
3-D-3	20.04	0.91	0.470	0.017	0.042	0.530	0.450	0.007	TR	TR	TR	TR
3-D-4	20.06	1.25	0.790	0.005	0.014	0.800	0.160	0.021	TR	TR	0.010	TR
4-D-1	19.99	0.85	1.090	TR	0.013	1.100	0.160	0.010	TR	TR	TR	0.005
4-D-2	19.90	0.61	0.630	TR	0.009	0.640	0.130	0.005	TR	TR	TR	TR
4-D-3	19.99	1.26	3.520	0.013	0.019	3.550	0.190	0.028	0.019	0.008	TR	0.007
1-E-1	20.01	2.00	0.120	0.009	0.022	0.150	0.120	TR	0.005	ND	TR	TR
1-E-2	20.11	1.60	0.068	0.008	0.017	0.093	0.190	0.007	0.005	ND	0.006	TR
1-E-3	20.12	0.95	0.078	0.005	0.007	0.085	0.099	0.009	0.005	TR	TR	TR
1-E-4	20.13	2.10	0.023	0.008	0.027	0.058	0.220	0.007	0.006	ND	0.009	TR
2-E-1	19.98	0.87	4.070	0.023	0.040	4.130	0.360	0.041	0.019	0.005	0.008	TR
2-E-2	20.01	1.42	0.190	0.014	0.036	0.240	0.270	0.005	0.017	0.005	0.016	0.007
2-E-3	20.16	1.26	0.110	TR	0.006	0.120	0.081	0.005	TR	0.011	0.006	TR
2-E-4	20.13	1.16	0.056	0.005	0.012	0.073	0.160	0.024	TR	TR	0.007	TR
3-E-1	20.03	1.62	0.120	TR	0.005	0.120	0.062	0.041	0.009	TR	0.007	0.009
3-E-2	20.02	0.95	0.150	0.014	0.059	0.220	0.520	0.017	0.019	TR	0.006	0.027
3-E-4	20.03	0.93	0.320	TR	0.007	0.330	0.094	0.100	0.038	0.009	0.007	0.006
4-E-3	20.14	1.23	2.060	0.006	0.013	2.080	0.200	0.048	0.011	0.007	TR	0.007
4-E-4	20.23	1.03	1.020	TR	0.006	1.030	0.074	0.043	0.019	0.009	TR	0.009
1-F-1	20.09	0.51	0.270	TR	0.007	0.280	0.100	0.005	0.006	TR	TR	TR
1-F-3	20.08	1.60	0.032	0.005	0.012	0.049	0.160	0.008	0.006	TR	TR	TR
1-F-4	20.28	2.14	0.044	TR	0.005	0.049	0.068	TR	TR	TR	0.007	TR
2-F-1	20.21	1.86	0.330	0.027	0.046	0.400	0.520	0.060	0.027	0.013	0.009	TR
2-F-2	20.21	1.77	0.230	TR	0.007	0.240	0.099	0.074	0.020	0.012	0.012	0.005
2-F-3	20.09	1.33	0.170	TR	0.012	0.180	0.110	0.260	0.034	0.007	TR	TR
2-F-4	20.04	1.41	0.150	TR	0.012	0.160	0.094	0.024	0.009	TR	0.011	0.006

TABLE 5 (cont'd). *Organochlorine residue levels in starlings, 1972*

Site No.[1]	Wet Weight, g	Lipid Weight, g	DDE	DDD	DDT	DDT/ Metabolites	PCB's [2]	Dieldrin	Heptachlor Epoxide	Oxychlordane	BHC	HCB
3-F-1	20.52	1.21	0.130	TR	0.014	0.140	0.150	0.072	0.017	0.007	TR	0.023
3-F-2	19.97	1.19	0.420	TR	0.012	0.430	0.130	0.012	TR	TR	TR	TR
3-F-3	20.03	1.54	0.370	0.032	0.080	0.480	0.840	0.017	0.008	0.006	0.012	TR
3-F-4	20.12	2.14	0.440	TR	0.019	0.460	0.190	0.033	0.007	TR	TR	TR
4-F-1[3]	20.10	1.09	1.060	TR	0.011	1.070	0.200	0.027	0.012	0.012	TR	0.025
4-F-3	20.13	1.10	0.620	TR	0.016	0.640	0.200	0.016	0.017	0.011	TR	TR
5-F-1	20.18	1.75	1.040	0.029	0.036	1.110	0.280	0.061	0.011	0.005	TR	0.008
1-G-2	20.15	1.26	0.230	0.008	0.022	0.260	0.220	0.027	0.009	TR	0.006	0.022
1-G-3	20.11	2.11	0.390	0.023	0.053	0.470	0.550	0.016	0.017	0.014	0.009	0.006
1-G-4	20.28	1.67	0.150	0.017	0.035	0.200	0.320	0.020	0.020	0.007	0.020	0.007
2-G-1	20.10	2.15	0.680	0.022	0.042	0.740	0.420	0.090	0.082	0.032	0.007	TR
2-G-2	20.01	2.21	0.110	0.006	0.013	0.130	0.100	0.280	0.077	0.016	0.006	TR
2-G-3	20.25	1.63	0.140	0.009	0.033	0.180	0.340	0.390	0.110	0.033	0.007	0.019
2-G-4	20.08	2.57	0.230	0.022	0.063	0.320	0.410	0.310	0.039	0.034	0.008	TR
3-G-1	20.04	1.49	0.550	0.025	0.029	0.600	0.210	0.260	0.034	0.014	0.006	0.011
3-G-2	20.05	1.04	0.220	0.012	0.077	0.310	0.720	0.035	0.057	0.028	0.008	0.014
3-G-3	20.04	1.14	7.950	0.044	0.049	8.040	0.220	0.110	ND	ND	TR	0.044
3-G-4	19.97	1.37	0.940	0.019	0.039	1.000	0.290	0.350	0.031	0.018	0.014	0.080
4-G-1	20.02	0.81	4.920	0.013	0.020	4.950	0.160	0.039	0.021	0.009	TR	0.024
4-G-2	20.09	0.92	0.680	TR	0.028	0.710	0.290	0.011	0.012	0.009	TR	0.009
4-G-3	20.11	0.84	0.710	TR	0.091	0.800	1.020	0.016	ND	ND	TR	0.044
4-G-4	20.29	1.71	11.700	0.089	0.046	11.800	0.220	0.150	0.065	0.018	0.011	TR
1-H-1	20.04	1.85	0.180	0.021	0.069	0.270	0.700	0.023	0.011	TR	0.007	0.007
1-H-2	19.96	1.26	0.680	0.054	0.059	0.790	0.370	0.023	0.008	0.008	0.005	TR
2-H-1	20.02	1.69	0.780	0.032	0.096	0.910	0.990	0.025	0.054	0.054	0.006	0.006
2-H-2	20.03	1.40	0.440	0.018	0.046	0.500	0.410	0.170	0.049	0.011	0.009	TR
2-H-3	20.04	1.15	0.560	0.011	0.026	0.600	0.250	0.340	0.031	0.007	TR	0.550
2-H-4	20.04	2.31	0.500	0.018	0.057	0.580	0.530	0.024	0.026	0.024	0.024	0.029
3-H-1	20.97	1.14	1.790	0.016	0.030	1.840	0.170	0.065	0.037	0.029	0.007	TR
3-H-2	20.00	1.79	0.130	0.020	0.049	0.200	0.520	ND	0.016	0.009	ND	0.140
3-H-3	20.06	1.16	0.440	0.006	0.031	0.480	0.370	0.030	0.011	0.012	TR	TR
3-H-4	20.07	1.28	0.660	TR	0.011	0.670	0.110	0.084	0.026	0.009	0.008	0.095
4-H-1	20.07	0.91	1.060	TR	0.022	1.080	0.290	0.310	0.091	0.100	TR	0.044
4-H-2	19.98	1.03	0.780	0.013	0.028	0.820	0.300	0.025	0.053	0.025	ND	0.059
4-H-3	22.04	1.06	0.890	0.840	1.560	3.290	19.900	0.029	0.071	ND	TR	TR
4-H-4	20.11	0.86	0.870	TR	0.013	0.880	0.250	0.280	0.028	TR	TR	TR
2-I-1	19.98	1.75	0.180	0.041	0.036	0.260	0.320	0.170	0.041	0.021	ND	0.210
2-I-2	20.05	1.79	0.500	0.046	0.065	0.610	0.650	0.730	0.150	0.034	0.012	0.280
2-I-3	20.02	1.44	0.260	0.009	0.031	0.300	0.250	0.028	0.024	0.010	0.018	0.046
3-I-1	20.02	0.77	0.370	0.016	0.042	0.430	0.470	0.076	0.023	0.025	TR	TR
3-I-2	20.03	0.94	1.090	0.009	0.040	1.140	0.440	0.160	0.011	0.009	TR	TR
3-I-3	20.01	0.90	0.150	0.006	0.016	0.170	0.160	0.028	0.008	0.006	TR	TR
3-I-4	20.90	0.77	0.570	TR	0.011	0.580	0.160	0.031	0.020	0.008	TR	0.007
4-I-1	20.03	0.88	5.040	0.015	0.024	5.080	0.190	0.050	0.041	0.012	TR	TR
4-I-2	20.00	1.07	0.600	0.011	0.053	0.660	0.860	0.022	ND	ND	TR	0.010
4-I-3	20.15	0.97	1.640	TR	0.037	1.680	0.410	1.200	0.014	0.038	TR	TR
5-I-1	20.02	0.78	0.460	TR	0.020	0.480	0.190	0.033	ND	ND	TR	TR
5-I-2	20.17	0.83	0.420	0.013	0.029	0.460	0.320	0.017	TR	0.011	ND	ND
2-J-1	20.08	0.45	0.380	0.008	0.021	0.410	0.230	0.120	0.022	0.015	TR	0.042
2-J-2	20.12	1.36	0.310	0.007	0.019	0.340	0.170	0.047	0.030	0.021	0.030	0.035
2-J-3	20.09	1.43	0.380	0.007	0.023	0.410	0.210	0.068	0.028	0.012	0.007	TR
2-J-4	20.09	2.02	0.150	0.007	0.016	0.170	0.200	0.011	TR	TR	TR	TR
3-J-1	21.21	1.12	1.110	0.014	0.039	1.160	0.390	0.530	0.038	0.035	ND	ND
3-J-2	20.05	1.05	1.610	0.008	0.056	1.670	0.520	0.130	ND	ND	TR	TR
3-J-3	20.01	1.25	0.530	0.031	0.046	0.610	0.540	0.097	0.021	0.027	ND	0.014
1-K-1	20.07	0.96	0.370	0.006	0.018	0.390	0.200	0.016	0.005	0.005	TR	TR
1-K-2	20.03	1.58	0.390	0.011	0.026	0.430	0.250	0.027	0.014	0.012	TR	TR
2-K-1	20.28	1.11	0.890	0.007	0.052	0.950	0.960	0.006	0.007	TR	0.005	0.008
2-K-2	20.22	1.17	0.250	0.012	0.026	0.290	0.290	0.021	0.019	0.019	TR	0.007

NOTE: Weights expressed in grams; residues expressed in ppm (μg/g) wet weight.
TR = trace.
ND = not detected.

[1] PCB levels estimated by examining peak between DDD and DDT with Aroclor 1254 as standard.
[2] Samples from each site composed of 10 birds except as indicated.
[3] Sample composed of 9 birds.
[4] Sample composed of 7 birds.
[5] Sample composed of 5 birds.
[6] Sample composed of 8 birds.

DIELDRIN

The difference between summer 1967 and winter 1967-68 dieldrin residue levels was much greater than that for DDT, and this seasonal difference was highly significant (Table 2). Residue levels the following fall were significantly lower than the summer/winter means. The vast majority of dieldrin residues found in the environment are derived from use of aldrin; aldrin/dieldrin sales (5) are roughly correlated with residue levels in starlings (Fig. 2). Results suggest that dieldrin levels may decline slightly in 1974 but should drop sharply in 1975 with the suspension of most uses of aldrin/dieldrin. Again, a more reliable fix on the slope will be generated from future collections.

Highest dieldrin residues (Table 4) were found in Washington (1-B-2), Idaho (1-B-1), Illinois (2-G-3), Iowa (2-G-4), Missouri (3-G-4), Indiana (2-H-3), Florida (4-H-1 and 4-I-3), Ohio (2-I-2), and North Carolina (3-J-1).

BHC

The compound BHC, including alpha, beta, and gamma isomers, was found in nearly all samples taken. Levels were extremely low; the highest was 0.036 ppm. BHC levels from the 1972 collection are not compared with those from past collections because HCB is being reported separately for the first time.

HCB

Although HCB has been used primarily outside the United States as a grain fungicide, it is possible that the compound has contaminated the environment in this Nation through industrial uses. In general, HCB levels were quite low, 0.1 ppm or less; almost half the samples had residues of 0.005 ppm or less. There were two sites which had high residue levels: 1-A-2 in Washington (3.330 ppm) and 1-B-1 in Idaho (2.340 ppm). Two other sites in Washington (1-B-2 and 1-B-3) had HCB levels exceeding 0.5 ppm.

HEPTACHLOR EPOXIDE

Nearly all samples collected in 1972 contained residues of heptachlor epoxide. Levels were relatively low, ranging from 0.005 to 0.210 ppm; only three sites had levels exceeding 0.1 ppm. Oxychlordane, which has been reported with heptachlor epoxide in the past, is being reported separately this year. Direct comparisons between previous heptachlor epoxide levels and the 1972 results are not made at this time.

OXYCHLORDANE

A breakdown byproduct of chlordane, oxychlordane, was found in nearly all samples at very low levels. The highest residue detected was 0.1 ppm.

PCB'S

Except for three sites, PCB's were found in all samples at levels below 1 ppm. Exceptions were sites 3-B-3 in Nevada, 1.87 ppm; 4-G-3 in Louisiana, 1.020 ppm; and 4-H-3 in Alabama, 19.9 ppm. The 1970 Alabama level was estimated to be 24.3 ppm; further monitoring is planned at this site to attempt to identify the source of contamination.

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Organochlorine Residues in Alaskan Peregrines[1]

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ABSTRACT

Organochlorine residue levels in eggs of Alaskan peregrines have remained essentially constant over the period 1969-73 despite decreased usage of these compounds in the United States and Canada. Studies on reproductive success in Great Britain and data on eggshell-thinning suggest that DDE residues above 20 ppm wet weight in peregrine eggs are associated with inability to maintain population levels. Residues in mainland Alaska are well above this critical figure and the reproductive rate is low. On the Colville River in northwestern Alaska, the last young falcons will fledge in 1975 and the remaining adult population will disappear by 1980 unless the present rate of reproductive failure is drastically and quickly reversed. In the Aleutians, however, levels range from 5 to 7 ppm and the reproductive rate is adequate to maintain the population.

Introduction

The decline of the peregrine *(Falco peregrinus)* has been one of the most dramatic events ascribed to the use of persistent pesticides (*1*). Although the species is too rare for specimens to be collected solely for analysis, a number of infertile or addled eggs and dead young have been obtained from Alaskan locales in recent years. This limitation on collection means that the data are not selected as randomly as researchers would like, a common problem with data on many top predators. Following restrictions on uses of organochlorines instituted in North America in recent years, residue levels of DDT and its metabolites in lower trophic levels have decreased (*2-5*). Because it has been predicted that organochlorine residues in higher trophic levels will continue to rise for several years after the input decreases (*6*), authors considered it important to examine levels in a top predator over this period.

Alaskan peregrines can be divided into two main groups: interior and maritime. The mainland population is highly migratory and winters in Central and South America (*1*); the maritime population is essentially resident (*7*). Although both populations are essentially bird eaters, each group preys upon different species. White et al. (*8*) found that 65 percent, by weight, of the food of Aleutian peregrines consisted of alcidae, which winter offshore in the Aleutians. Residue levels of DDE ranged from 0.001 to 0.094 ppm wet weight for eight individuals of four alcid species (*7*). Truly migratory species comprised less than 3 percent of the prey.

Cade et al. (*9*) found that migratory waterfowl comprised half the food of the peregrines along the Yukon River; shorebirds and gulls represented about one quarter. Only one major prey species, the Canada jay *(Perisoreus canadensis)*, is nonmigratory. In 1966 this species accounted for 11 percent by weight of the prey observed at aeries. A similar pattern was exhibited on the Colville River in 1967-69: of more than 45 species of prey found at aeries, only Ptarmigan *(Lagopus lagopus* and *L. mutus)* are permanently resident in Alaska. The Ptarmigan comprise only 14 of 433 prey species (*10*).

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Thus the mainland population not only migrates into areas of heavy pesticide use, but most of its prey species are also migratory. On the other hand, because Aleutian peregrines have little direct contact with pesticides, their levels reflect the background contamination of the North Pacific.

Methods

In most cases eggs were blown by routine oological methods and the contents were immediately preserved in 10 percent formalin. If possible, eggs were rapidly shipped intact. Expression of residue levels on a wet-weight basis requires that all eggs be at the same stage of development and weighed shortly after collection. These conditions cannot be met for much of the field work in Alaska. Therefore, authors prefer to use the oven-dried weight. The amount of extractable fat was measured so that results could also be expressed on a lipid-weight basis. To compare results to those in much of the published work, divide ppm dried weight by 5 to give the wet-weight value.

Samples were dried for 48 hours at 45°C and then ground with coarse anhydrous Na_2SO_4. Samples were extracted in Soxhlet thimbles for 8 hours with a 1:3 mixture of ethyl ether:petroleum ether. A florisil column was used to remove fats and other interfering substances. A varian aerograph gas chromatograph equipped with ^{63}Ni electron-capture detectors and two 0.6-cm-by-1.8-m columns was used for pesticide quantification. Liquid phases and solid supports were 2 percent QF-1 on 40/50 Anakrom ABS and 5 percent SE-30 on 60/80 Chromosorb W. Operating conditions were:

Temperatures:	Inlet	225° C.
	Detector	275° C.
	Column	200° C.
Carrier Gas:	Dry Nitrogen.	

Polychlorinated biphenyls (PCB's) were quantitated on two peaks after saponification. Recovery rates were 85 to 95 percent and values were not corrected.

Results and Discussion

Levels of DDE found in peregrine eggs during 1968-73 are listed in Table 1. There is no indication of any change in residue levels for either the interior or maritime populations. Small sample sizes and the nonrandom nature of the collections preclude statistical analysis. A few individual eggs were collected from the same site in different years, so comparisons can be made on a site basis. Two eggs from cliff 68 on the Colville River had DDE levels of 146 and 199 ppm oven-dried weight and shell index figures of 1.57 and 1.27 in 1968; an egg from this site in 1971 had a DDE level of 174 ppm and a shell index of 1.54. Shell index represents weight (mg) divided by the product of the length and breadth (mm) of the empty eggshell (*11*). In 1968 at Shivugak, on the Colville, the residue level was 276 ppm with an index of 1.57. In 1971 two eggs from this cliff had values of 215 and 352 ppm with index values of 1.46 and 1.37. Thus, neither from a consideration of individual sites nor from overall averages is there any evidence of a decrease in residue levels.

Ten young peregrines were found dead in aeries along the Colville River in 1969; eight were found in 1971 (*12*). Nine of the 1969 young but none of the 1971 young could be analyzed. Residue levels in the muscle, liver, and brain are given in Table 2. These values are compared with those found in four young collected in 1966 (*9*), although they are not strictly similar. The 1966 specimens were alive when collected from various places, whereas the 1969 sample consisted of young found dead in the nest, apparently having starved after abandonment. Starvation may account for the higher residue levels in the brain in 1969. Nevertheless, even the highest brain levels, 42 ppm dry weight, are low compared to levels normally considered lethal (*13*).

TABLE 1. *DDE levels in Alaskan peregrine eggs, 1968-73*

Area	Year	DDE [1]			Shell Index			Thinning, %	Significance of Thinning
		Number	Mean	St. Dev.	Number	Mean	St. Dev.		
INTERIOR ALASKA									
Colville River	1968	11	193.9	159.8	11	1.42	0.13	24.9	<0.001
	1969	5	163.8	87.4	5	1.53	0.15	23.5	<0.01
	1971	7	210.8	92.0	7	1.49	0.09	21.2	<0.005
Yukon River	1968	11	105.6	53.0	11	1.49	0.10	16.8	<0.001
Tanana River	1969	3	344.3	81.0	3	1.42	0.14	20.2	ND
	1973	3	302.7	84.1	3	1.44	0.18	19.1	ND
ALEUTIANS									
Amchitka	1969	6	25.0	3.6	6	1.74	0.10	7.4	<0.01
	1970	6	39.8	26.4	6	1.73	0.21	8.0	<0.05
	1971	3	24.1	15.1	3	1.73	0.19	8.0	ND
	1973	7	26.3	9.2	7	1.72	0.16	8.3	<0.05

NOTE: Pre-1946 values used to calculate percentage thinning for the various areas are: Colville 1.89, Aleutians 1.88, and Yukon 1.78; the value for the Yukon is probably too low (*12*). Data for the Colville 1968 and 1969, Yukon 1969, and Amchitka 1969 and 1970 have been reported previously (*12*) but not on a year-by-year basis.
ND = no data; sample too small.
[1] Residues are ppm oven-dry weight.

TABLE 2. *DDE levels in young peregrines found dead in aeries along Colville River, Alaska*

Tissue	1969 [1]		1966 [2,3]	
	Mean St. Dev.	Range	Mean	Range
Muscle	5.1 ± 2.0	1.2-19.0	6.3	0.8-14.6
Liver	11.7 ± 4.0	1.2-33.0	1.6	1.3- 1.9
Brain	17.6 ± 4.7	1.1-42.0	1.6	0.5- 3.0

NOTE: Residues are ppm oven-dry weight.
[1] Samples of all tissue represent nine individuals.
[2] Samples of all tissue represent four individuals.
[3] See Literature Cited, reference 9.

The possibility that organochlorines were involved in the failure of parental care remains to be explored; abnormal behavior of adult falcons at their aeries certainly appears to have increased in recent years.

Three clutches of peregrine eggs laid in captivity during the Cornell breeding project have also been analyzed for residues. Eggs from a bird taken as a nestling from the Colville River in 1968 had DDE levels of 7.8 ppm dry weight and a shell index of 1.82 in 1972. Eggs from a Yukon River bird taken as a nestling in 1966 and raised on a diet of fresh fowl and coturnix quail had DDE residue levels of 9.0 ppm in 1972 and 7.7 ppm in 1973. Shell index figures were 1.79 and 1.80, respectively. The bird's controlled diet of fowl and quail thus resulted in low residue levels and a shell index approaching levels common before application.

PCB levels follow quite a different pattern from those of DDE (Table 3). In the Alaskan interior, the ratio of total DDT to PCB's is almost 1:1, whereas in the Aleutians the ratio is down to about 1:5. No other organochlorines were detected above trace amounts.

TABLE 3. *PCB levels in peregrine eggs, Alaska*

Area	Year	PCB			ΣDDT: PCB
		Number	Mean	St. Dev.	
INTERIOR ALASKA					
Colville River	1971	7	173.4	54.9	1.22
Tanana River	1973	3	350.1	256.9	0.66
ALEUTIANS					
Amchitka	1971	3	114.4	77.4	0.20
Amchitka	1973	7	144.6	68.3	0.18

NOTE: Residues are ppm oven-dry weight.

EFFECT OF ORGANOCHLORINE RESIDUES

The relation between DDE residues in eggs and the thickness of eggshells of Alaskan peregrines was plotted in 1971 (*12*). Data from the present study which are plotted in Figure 1 confirm the original plot. It is significant that residues from the lightly contaminated eggs of captive birds closely fit the regression line. A decrease in thickness of 20 percent or more is associated with population declines (*14*); in the peregrine this critical thickness corresponds to about 20 ppm wet weight DDE in the eggs. Equivalents for dry weight and lipid are 100 and 500 ppm, respectively. Residues in eggs do not affect shell thickness, however; they are used merely as convenient indicators of circulating levels in mother birds at the time of egg maturation.

Direct embryonic effects of DDE are probably unimportant, because high levels are necessary to affect reproduction in species in which eggshell thinning does not occur and when the eggs are incubated artificially (*15,16*). PCB's appear to be considerably more embryotoxic than DDE (*17*).

It is not clear whether eggshell breakage is purely the result of structural failure, or whether it is caused by the mother bird's abnormal behavior on the nest. Ratcliffe (*18*) feels that the behavioral component may be quite important. In the bird's diet, DDE levels of 40 ppm (*19*) and PCB's of 10 ppm (*17*) have been shown to cause behavioral changes leading to decreased reproductive success in ringed turtle doves *(Streptopelia risoria)*.

Ideally, one would like to determine what level of organochlorine residues in peregrine eggs interferes with the productivity necessary for a stable population. The best available data are from Great Britain. Ratcliffe showed that in 1962 reproduction was low in England, Wales, and southern Scotland, and that only in the Highlands of Scotland were peregrines reproducing normally (*18*). In southern England only 3 percent of the sites had young who hatched. The rate in Wales was 4 percent; in nothern England, 7 percent, and in southern Scotland, 5 percent. In the Highlands of Scotland 38 percent of the sites had young who hatched. By 1971 substantial improvement had occurred in northern England and southern Scotland, but reproduction was still poor in Wales and southern England. In 1971 the rate of sites hatching young was 7 percent in southern England, 4 percent in Wales, 24 percent in northern England, and 24 percent in southern Scotland. In the Highlands, this index of productivity remained essentially constant. Total organochlorine pesticide residue levels in eggs from northern England declined from 24.8 ppm wet weight in 1962-66 to 7.9 ppm in 1967-71.

Corresponding values for southern Scotland were 14.5 and 11.0 ppm. Values for the Highlands were below 10 ppm throughout; no values are available for southern England or Wales for either period. About 90 percent of the residues are DDE. Nevertheless, other compounds, especially dieldrin, remain a problem.

Lockie et al. noted that, concurrent with an increase of breeding success of the golden eagle *(Aquila chrysaetos)*, mean levels of dieldrin decreased from 0.86 to 0.34 ppm (*20*). This correlation does not apply to the

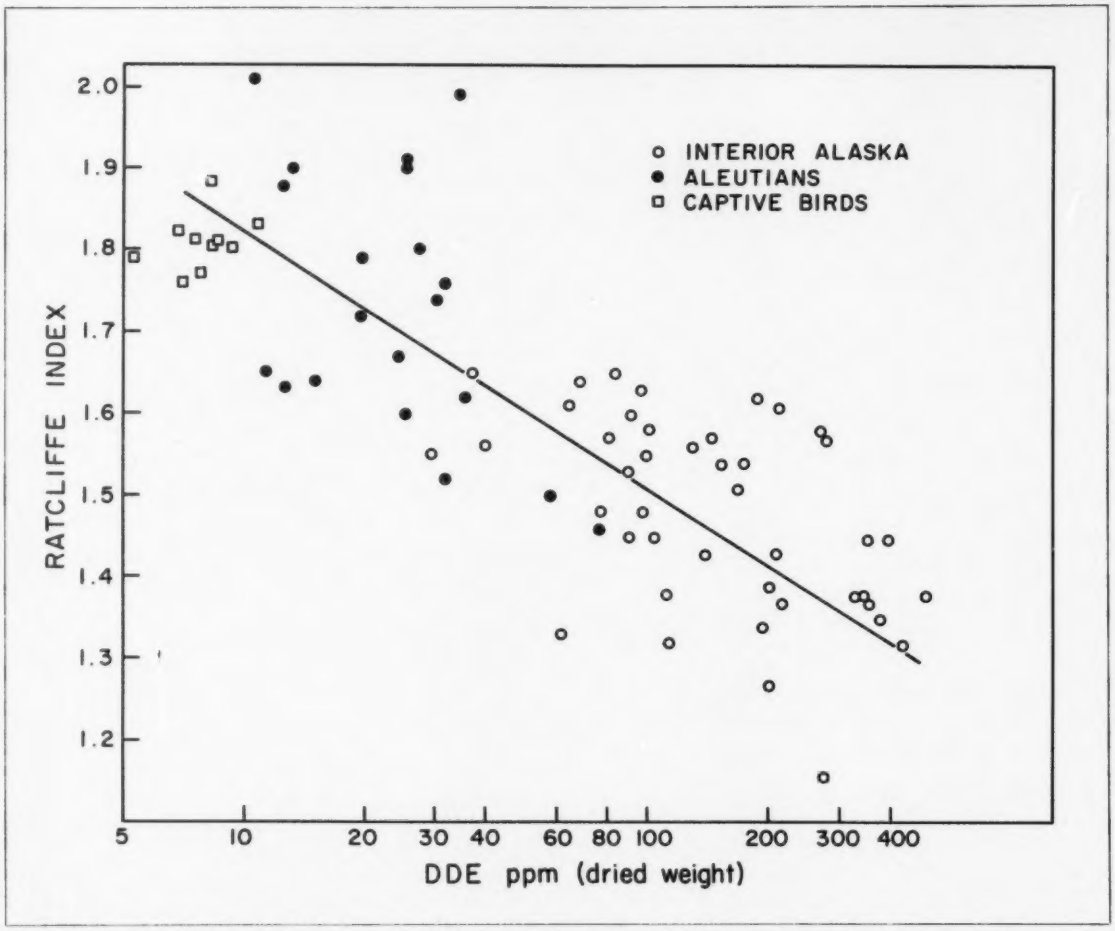

FIGURE 1. *Relation between shell thickness index and DDE residues in eggs of Alaskan Peregrines.*

peregrine. Ratcliffe's data show that the highest mean level of dieldrin, 1.2 ppm, occurred in the Highlands in 1962-66 when the peregrine was reproducing well (*19*). Residue levels in northern England decreased from 1962-66 to 1967-71, but they increased in southern Scotland.

Although the residue levels represent 5-year periods, and the information on reproductive performance represents single years, and residue levels are not related to reproduction at the specific aeries from which the eggs were collected, a tentative conclusion can be formed: namely, that the critical level of DDE in egg content is about 15 to 20 ppm wet weight. This value corresponds with the suggested critical value of 20 ppm DDE, wet weight, derived from consideration of the eggshell-thinning data. These lines of evidence indicate that peregrines should continue to maintain normal population levels in the Aleutians where wet-weight means of egg content are 5 to 7 ppm, but not in the Alaskan interior populations where wet-weight means are 20 to 40 ppm. This hypothesis agrees with published observations of peregrines in the Aleutians (*8*) and interior Alaska (*10,12,21*) on reproductive success and population changes. As shown in Table 4, this relationship is particularly dramatic for peregrines nesting on the Colville River. If the present rate of reproductive failure is not drastically reversed soon, the last young falcons will fledge from the Colville aeries in 1975, and the remaining adult population will slowly disappear by 1980.

The use of DDT in the United States has decreased almost linearly from a peak of 78 million pounds in

1959 to essentially zero in 1973 (*22*). Various monitoring surveys have clearly indicated decreased levels of DDT and its metabolites over this period. Residue levels in estuarine mollusks surveyed from 1965 to 1972 showed a clear trend toward decreased levels of DDE beginning in 1969-70 (*2*). In 1970 Martin and Nickerson found that residue levels in starlings *(Sturus vulgaris)* had decreased from 1967-68 levels at 35 of 38 sampling points (*4*); overall reduction of total DDT was 53 percent. Henderson et al. found that total DDT residues in fish had decreased at 33 of 50 sampling points from 1968 to 1969 (*3*). Ware et al., while studying the effect of a 2-year moratorium on the agricultural use of DDT in Arizona, found that levels in alfalfa and beef fat decreased significantly, but soil levels changed only negligibly (*5*). The rate of clearance indicated by these studies appears to be more rapid than had been predicted by Harrison et al. in 1970 (*6*); they estimated that the half-life of DDT for a given trophic level would be four times the average life span of the longest-lived species.

TABLE 4. *Number of breeding pairs and productivity of peregrines, Colville River, Alaska*

Year	Total No. Pairs	No. Pairs Producing Young [1]	No. Young Produced [1]
1952-59 [2]	32-36	20-25	40-50
1967 [3]	27	18	34
1968 [3]	32	16	34
1969	33	13	26
1971 [4]	25	9	14
1973	14	4	9

[1] Ranges are estimated. The entire river was not monitored every year.
[2] Refer to Literature Cited, reference 26.
[3] Refer to Literature Cited, reference 12.
[4] Refer to Literature Cited, reference 10.

Samples of a few flickers *(Colaptes auratus)* killed by migrating falcons in Maryland and Virginia had residue levels of only a trace to a few tenths of a ppm. Flickers, which migrate the same time as the falcons, are an important food source for peregrines. The fact that levels of organochlorines in arctic peregrine eggs remain high suggests that these residues are obtained largely in Central and South American countries where their use has not been banned.

Although the use of DDT in the United States, Canada, and many European counties has decreased considerably, there is no clear evidence that use is decreasing on a global scale. United States production of DDT remained between 100 and 180 million pounds from 1955 to 1970 and a steadily increasing proportion of the DDT was exported (*22*). Many countries in Central and South America, Africa, and Asia now manufacture DDT. Monitoring levels of organochlorines in ocean plankton would trace the concentration of total DDT in the world's ultimate sink.

Findings of the current study cause little optimism about the ultimate fate of North American peregrines. Residue levels remain high and reproduction low in mainland Alaskan peregrines. There is little to suggest that the 1970 forecast of extinction within a decade (*21*) was incorrect for some of the northern populations, and the same bleak picture applies to the remaining Rocky Mountain population (*23*). The situation in Greenland, fortunately, appears more encouraging (*24*).

The first major success in artificial breeding occurred in 1973 when 20 young peregrines were raised; two females from the Colville River mothered 13 of those 20 hatchlings (*25*). This was more than the entire natural productivity from the Colville River in 1973. Authors' findings suggest that reintroduction of captivity-produced peregrines will be successful only if the released falcons do not migrate south of the United States.

Acknowledgments

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GENERAL

Comparison Between Two Methods of Subsampling Blubber of Northern Fur Seals for Total DDT Plus PCB's[1]

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ABSTRACT

Samples of 100 g blubber were collected from each of twelve 8- to 13-year-old fur seals (Callorhinus ursinus) *taken off the coast of Washington State in March 1972. Two methods of subsampling the blubber were compared. The mean level of total DDT (DDE, DDD, and DDT) plus polychlorinated biphenyls (PCB's) from a 5-g chunk of blubber taken from a 100-g sample was significantly less than the mean level from a 5-g subsample taken from the remainder of the blubber sample after it had been thoroughly ground. Total DDT plus PCB residues ranged from 5.66 to 72.17 ppm, with a mean of 23.69 ppm in the chunks, and from 5.33 to 95.70 ppm, with a mean of 28.64 ppm in the homogenized blubber.*

Introduction

Northern fur seals (*Callorhinus ursinus*) breed each summer on islands in the Bering and Okhotsk Seas, where they are harvested for their furs. Small breeding colonies are found on the Kuril Islands, Japan, and the Channel Islands off southern California. Fur seals are pelagic except during the breeding season. Their range extends from California to Japan.

In the sampling of marine mammals for pesticide residues the size of some organs and the blubber layer makes it necessary to take not only a relatively small sample from each animal, but also a subsample. Methods of subsampling tissues from marine mammals for pesticide residues have varied widely. Holden and Marsden (*1*) used 5-g aliquots of tissue from an original sample of unspecified weight. Anas and Wilson (*2*) and Aucamp et al. (*3*) collected and analyzed 10 g tissue; Arndt (*4*) collected 15-100 g tissue and analyzed 10-g subsamples. Wolman and Wilson (*5*) collected 100 g tissue and analyzed subsamples of unspecified weight. The present report compares total DDT (DDE, DDD, and DDT) plus PCB (polychlorinated biphenyl) residues from two methods of subsampling northern fur seal blubber to see whether the subsampling method affects results.

Analytical Methods

Two methods of subsampling the blubber were used: removing and analyzing a random 5-g chunk of frozen blubber from a 100-g sample; and grinding the remainder of the 100-g sample while frozen, stirring thoroughly, and removing and analyzing a random 5-g subsample. The 100-g sample of blubber consisted of a cross section taken from the belly area near the midline and anterior to the mammaries of 12 adult female northern fur seals taken off the coast of Washington State in March 1972. Samples were kept frozen at −23° C.

Ages of the seals, determined by counting lines of dentine in longitudinally sectioned upper canine teeth (*6,7*), ranged from 8 to 13 years. Both parous and nonparous seals were included. Unpublished data by the authors on 51 adult female northern fur seals ranging from 8 to 13 years have shown that mean organochlorine residues are not associated with age or parous condition ($P > 0.05$), so pregnant and nonpregnant seals from 8 to 13 years were pooled for the current study.

Organochlorine residues were determined by WARF Institute, Inc., Madison, Wisc. Methodology has been described previously; total DDT and PCB's were summed to reduce possible errors (*8*).

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Results and Conclusions

Total DDT plus PCB's ranged from 5.66 to 72.17 ppm, with an average of 23.69 ppm in the chunks, and 5.33 to 95.70 ppm with an average of 28.64 ppm in the homogenized blubber (Table 1). A paired t-test indicated that the average total DDT plus PCB level for samples from homogenized blubber was significantly greater than the level for chunks ($P < 0.05$). Comparison of values in Table 1, however, suggests that the difference in results between the two sampling methods increases with increasing residue levels. The average difference of 4.95 ppm, therefore, may not be strictly applicable to the range of residue levels observed in this sample of 12 individuals.

TABLE 1. *Total DDT plus PCB's in blubber from 12 adult female fur seals, Washington State, March 1972*

Sample No.	Type of Sample		Difference	Ratio
	Chunks	Homogenized		
1	5.66	5.33	−0.33	1.08
2	8.40	11.79	+3.39	0.71
3	14.78	16.68	+1.90	0.89
4	17.15	17.34	+0.19	0.99
5	15.05	17.93	+2.88	0.84
6	17.60	17.96	+0.36	0.98
7	20.90	25.27	+4.37	0.83
8	25.86	28.04	+2.18	0.92
9	26.55	28.96	+2.41	0.92
10	16.73	29.78	+13.05	0.56
11	43.47	48.89	+5.42	0.89
12	72.17	95.70	+23.53	0.75
Average	23.69	28.64	+4.95	0.83

NOTE: Data expressed in ppm; mg/kg wet weight.
Ages ranged from 8 to 12 years.

Ratios of residue values (chunk:homogenized) in Table 1 do not exhibit a trend with increasing residue levels. This hypothesis was indirectly tested by computing a weighted regression of residue values from chunks on those from homogenized samples and comparing the estimated intercept with zero. The variance about the line was assumed proportional to the residue level, so weights used in the regression were constructed from reciprocals of residue values for homogenized samples and adjusted to sum to the sample size of 12. The intercept and its standard error were estimated to be 1.60 and 3.98, respectively. Because the standard error of the intercept is nearly 2.5 times larger than the intercept itself, there is little reason to reject the hypothesis that the intercept is zero. Therefore it appears that residue values from chunks are a constant fraction of those from homogenized samples and that a regression through the origin adequately describes the relationship between results from the two sampling methods.

Again, assuming the variance proportional to the residue level, the slope of the above regression is best estimated from the ratio of the average for chunks to the average for homogenized samples This value, 0.83, is significantly less than 1 ($P < 0.05$) and indicates, as did the paired t-test, that significantly different residue values were obtained from the two subsampling methods used in this experiment (*9*). Analyses of residue levels expressed on a fat basis rather than a wet-weight basis produced the same results.

The reason for the differences in pesticide levels by the two methods is not known. Obviously, one or both of the methods was not random. Differences could be caused by uneven distribution of organochlorine compounds or lipids in the blubber, or unequal separation of these compounds during subsampling. It is known, for example, that in finback whales (*Balaenoptera physalus*), the percent lipids in three sections of blubber is highest in the outer section and lowest in the inner section (*10*). Whatever the reason for the differences, this study demonstrates that careful consideration should be given to the way in which subsamples are taken for pesticide analyses.

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Degradation of Parathion Applied to Peach Leaves

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ABSTRACT

Parathion was applied to peach trees in three different formulations 70 days before harvest. Leaf samples were taken periodically through the 70-day period and gas-liquid chromatographic analyses were conducted for dislodgable and penetrated residues. Analyses were also conducted for paraoxon and the s-ethyl isomer of parathion. Punched samples were compared to whole-leaf samples; generally residue levels for both types corresponded closely. A new experimental formulation, encapsulated parathion, produced highest levels of total parathion throughout the 70-day study, but even this formulation resulted in low total residue levels around 1 ppm at time of harvest. Degradation of the s-ethyl isomer of parathion was generally very rapid in all formulations studied. Dislodgable residues of paraoxon may be significant in some formulations and should be included in parathion degradation studies. Much of the parathion found on peach leaves throughout the growing season was dislodgable residue, but this depended considerably on the formulation used.

Introduction

Recent reports (*1-6*) have shown that foliage and other plant parts may accept and retain deposits of pesticide residues in much greater quantities and for longer times than does fruit, and that foliage may be a very important factor in considering worker reentry into insecticide-treated orchards. Gunther et al. (*7*) observed that a freestone peach tree about 10 years old has a leaf-to-fruit surface area ratio approximating 53:1; the same ratio for a clingstone peach tree is 28:1. Because foliage appears to be the greatest source of exposure of potentially toxic insecticides to farm workers, authors of the present study aimed to ascertain leaf residue levels of parathion and its toxic degradation products.

Formulations can have an appreciable effect on deposit and penetration levels as well as toxicity of insecticides (*3,8,9*). This study compares residue levels of two commonly used formulations, emulsifiable concentrate (EC) and wettable powder (WP), and an experimental formulation, encapsulated parathion (Enc.). Both dislodgable and penetrated residues were measured periodically for 70 days following application of each formulation. EC and Enc. formulations were applied July 10, 1971, and the WP formulation was applied August 3, 1971.

El-Rafai and Hopkins (*10*) reported that paraoxon and possibly the s-ethyl isomer of parathion accumulated on both grass and leaf surfaces and were principal metabolites within the plant. The first few days after treatment, according to these investigators, paraoxon accumulated faster on leaf surfaces than it did internally. The adverse was true several days later, however: surface paraoxon degraded more rapidly. Both paraoxon and the s-ethyl isomer are stronger cholinesterase inhibitors than parathion, which in accumulated amounts could pose a threat to workers through dislodgable deposits. Therefore, the study reported here includes both these products as well as their parent compound, parathion.

Analyses were conducted on punches taken at or near the center of leaves and on the whole leaf. Results

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were compared on a weight basis. This portion of the study was designed to determine whether punched grape leaves would be representative for expressing dislodgable residue in $\mu g/cm^2$ without sacrificing accuracy to sampling.

Volunteer workers were permitted to enter the fields a few days following parathion application; samples of blood and urine were taken before and after their entrance into the fields. Because this study involves only residues on peach foliage, findings involving human subjects will be reported elsewhere (*11*).

Materials and Methods

FIELD APPLICATION AND SAMPLING

A 60-acre orchard of freestone peaches southwest of Modesto, Calif., was subdivided into three 20-acre plots. Parathion was applied to each plot in one of the three formulations mentioned above: WP, EC, or Enc. The latter formulation encloses parathion in a porous microplastic capsule. This permits parathion to be released more slowly, over a longer period of time, than are most conventional insecticide formulations.

The formulations were applied with a ground sprayer at rates of 1 lb active parathion per acre for both the EC and Enc., and 2 lb per acre for WP. Parathion was applied at 400 gallon/acre for each of the three 20-acre plots, which is a standard application for peaches in most counties of California. In all three applications, sulfur was also mixed with the formulations and applied at a rate of 20 lb active sulfur per acre. Each 20-acre plot was subdivided into four replicate plots. Ten trees near the center of each replicate were selected for sampling. Whole-leaf and 2.5 cm^2 leaf-punch samples were taken one day before application, the day of application, and 3, 7, 14, 21, 28, and 70 days afterward. Twenty leaves and punches were taken from each tree selected at random in a circular fashion at approximately 18° intervals, 5 feet above ground. Samples from each 10-tree plot were combined, labeled, and frozen immediately in dry ice. Samples were soon transferred to a walk-in freezer where they were kept frozen at subzero temperatures until analyzed.

EXTRACTION AND ANALYSIS

Samples of punched leaves were weighed and the grams per sample were recorded with the total number of punches. Whole-leaf samples were handled on a weight basis only and no attempt was made to measure leaf area. Each sample was extracted for dislodgable residue and for remaining residue according to the method of Gunther (*7*). Using this procedure, 200 leaf punches were transferred to a heavy-walled 500-ml Erlenmeyer flask. To each flask was added 200 ml of a 1:25,000 dilution of Sur-Ten wetting agent, also called aerosol OT 75 (trimethyl laurel ammonium chloride). Contents of the flask were shaken for 60 minutes on a Gyrotory shaker at 180 rpm. The aqueous solution was decanted into a 1-liter separatory funnel and another 200 ml diluted wetting agent was added. The solution was shaken for 30 minutes. The second portion of the wash liquid was combined with the first portion and a final 25 ml of wash solution was added to the leaves and shaken for 5 seconds. All Sur-Ten wash solutions were combined and extracted for 30 seconds with four 200-ml portions of chloroform. After filtering through sodium sulfate the organic solvent extracts were combined and stored in the dark until analyzed.

The remainder residue, that which had penetrated, was extracted by transferring leaf contents remaining from Sur-Ten washings to a Waring blender container with 200 ml chloroform. Forty g sodium sulfate was added and the contents were blended for 2 minutes. The solvent was filtered through Whatman No. 1 filter paper into a storage bottle containing 20 g sodium sulfate. An additional 200 ml chloroform was added to the blender cup and the contents were blended for 30 seconds and filtered. The extraction was repeated for 30 seconds with 200 ml chloroform, filtered, and the combined chloroform extracts were stored in the dark until analyzed.

Whole-leaf samples were handled as the punched samples had been. A 50-g portion of leaves was washed twice with 450 ml Sur-Ten solution in a 1-liter flask, then washed again with a 100-ml solution. The solvent extraction was carried out by transferring 100 ml Sur-Ten wash solution representing 5 g leaves into a 250-ml separatory funnel and extracting four times with 50 ml chloroform. The remaining residue was handled in the same manner as the punches except that a larger quantity of sodium sulfate was added to the blending operation: 100 g instead of 20 g.

To remove residues from fruit samples, four peaches were selected, weighed, and measured, taking the diameter of each peach through three mutually perpendicular axes. Surface area was calculated by averaging the diameters and assuming the peach was a sphere. The four peaches were transferred to a 1-gallon can, sealed with 500 ml Sur-Ten solution, and rolled for 1 hour. The wash solution was decanted and the peaches were given a final wash with 500 ml Sur-Ten solution for 30 minutes. Washes were combined and an aliquot equivalent to 50 g was extracted as described for leaf samples. Remainder or penetrated residues were extracted by chopping only the edible portion of the fruit in a Hobart food cutter. Fifty-g chopped peaches were transferred into a blender containing 50-g sodium sulfate. Two hundred ml chloroform was added to the blender and the contents were blended for 2 minutes. The extraction process was then handled according to the procedure discussed for remaining residue in leaf tissue.

LABORATORY ANALYSIS

Because leaf samples contained high levels of sulfur, which interferes with the analysis of parathion, paraoxon, and the s-ethyl isomer of parathion, the extract had to be cleaned for detection by gas-liquid chromatography (GLC). It was also desirable to develop a procedure by which paraoxon and the s-ethyl isomer could be separated from parathion prior to gas chromatography. Most GLC columns do not satisfactorily separate these materials, particularly when parathion has considerably more residue than the other two products. As a result there is an overlapping of GLC peaks which prevents satisfactory quantitative results.

The cleanup procedure involved column chromatography using florisil as the adsorbant. A glass column, 2 cm in diameter and 12 cm long with a 150-ml reservoir, was packed with 8 g PR grade florisil and prewashed with 50 ml benzene. An extract of the sample in chloroform was evaporated to dryness and redissolved in 5 ml benzene. The sample was quantitatively transferred to the column and eluted with 50 ml benzene; the eluate caused an interfering sulfur response which was discarded. Eighty ml 5 percent ethyl ether by volume in benzene was transferred to the column; this fraction contained the parathion that was collected. The column was then eluted with 75 ml 8 percent acetone in benzene; this fraction contained paraoxon and the s-ethyl isomer of parathion. Depending on the quantity of residue present, the sample was evaporated to dryness and the volume was adjusted to facilitate gas chromatographic analysis.

Analyses were carried out with a Varian Aerograph Model 204 gas chromatograph equipped with a cesium bromide thermionic detector. Two gas chromatographic columns satisfactorily separated the three products. One column was a 2-ft-by-⅛-in.-OD pyrex glass column packed with 5 percent (w/w) Dexsil 300 on 80/100 mesh Gas Chrom Q; the other column was a 2-ft-by-⅛-in.-OD pyrex glass column packed with 5 percent Apiezon L on Gas Chrom Q, 80/100 mesh. Both columns were operated at 225° C with a slightly higher injection and detector temperature. Gas flow conditions were 19 cc/min for nitrogen, the carrier gas; 16 cc/min for hydrogen; and 150 cc/min for air.

Recovery studies for parathion, paraoxon, and the s-ethyl isomer of parathion were performed before and during the study. Samples of control leaves were taken from plots prior to application and were fortified on leaf tissues during extraction before addition of surfactant solution. Samples of control peaches were taken at harvest from trees not sprayed with parathion. Two levels of fortification at 0.1 and 1.0 ppm were made for each chemical analyzed. All recovered residues were based on total residue: that found in the surfactant solution plus the remainder found in the chloroform extract.

Results and Discussion

The method employed to separate and detect parathion, paraoxon, and the s-ethyl isomer of parathion on and in peach leaves and fruit is reproducible and can detect residues as low as 0.01, 0.02, and 0.02 ppm, respectively, for each of the three chemicals. Fortified control studies at the 0.1 and 1.0 ppm level ranged between 90 and 100 percent, 85 and 95 percent, and 70 and 85 percent, respectively, for parathion, paraoxon, and the s-ethyl isomer. None of the data reported were based on or corrected for percent recovery. Residues found were frequently confirmed by repeated analysis and by using both the Apiezon L and the Dexsil 300 columns. Further confirmation would have been desirable through gas-liquid chromatography/mass spectrometry and other detection systems; however, such instrumentation was not available.

Recent reports (*5,7*) have shown that dislodgable residue is the principal means by which agricultural workers are exposed to pesticides. There are two means of measuring this dislodgable portion of the pesticide: one uses a weight basis in which data are usually reported in ppm; the other involves surface area only and is expressed as $\mu g/cm^2$. Figures 1-3 illustrate the difference between expressing data as ppm and as $\mu g/cm^2 \times 10^{-2}$. Taking into consideration normal field and laboratory variability, there appears to be very little difference between the two measurements with peach leaves. This is likely a result of the uniform density of the peach leaves. Once such uniformity has been established, data can be expressed in either form so long as one remembers that ultimately all dislodgable residue data must be understood in terms of surface residue to which a worker may be exposed. Table 1 compares this relationship with a final standard deviation between individual samplings for the ratio of ppm/$\mu g\ cm^2 \times 10^{-2}$. For each formulation the standard deviation did not exceed 0.09.

The most practical way of measuring the dislodgable residue on surface foliage is through a representative punched sample. On the other hand, the punched sample is usually taken near the center of the leaf or foliage. This may not be representative of the total leaf surface because on high-volume applications some investigators have observed that residues on peach leaves appear to have their greatest deposition on the periphery of the leaf, particularly the tip. Therefore this study involved both whole-leaf sampling and punch sampling. Figures 4-6 show total and dislodgable residues expressed on a weight basis (ppm) of the whole-leaf versus the punched samples for each of the three formula-

tions. In all three formulations total residues found were similar in both types of sampling; yet the dislodgable portion of the total residue appeared to differ depending on whether punched or whole-leaf samples had been taken. It is difficult to understand why this difference exists, but current studies indicate that higher dislodgable residues in punched samples are primarily due to the extraction procedure, which is slightly different from that of whole-leaf samples in the ratio of surfac-

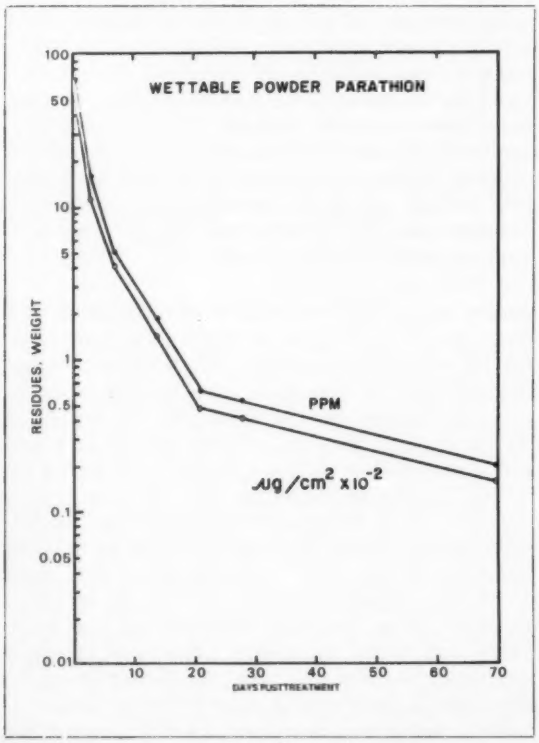

FIGURE 1. *Parathion residues from punched peach leaf samples following application of wettable powder formulation at 2 lb a.i./acre*

tant to total crop material. Until this difference can be resolved it is recommended that punched samples be used for analysis of dislodgable residues.

When dislodgable residues are discussed for the encapsulated formulation, they do not indicate residue levels to which a worker may be exposed: the capsule minimizes actual dermal exposure of the worker to the pesticide while extending the residual life of the active ingredient. The extraction procedure in this study removed the microcapsule containing the insecticide and any other residue that might be considered dislodgable from the leaf surface. Once the encapsulated product has been removed, the pesticide contained in the capsule

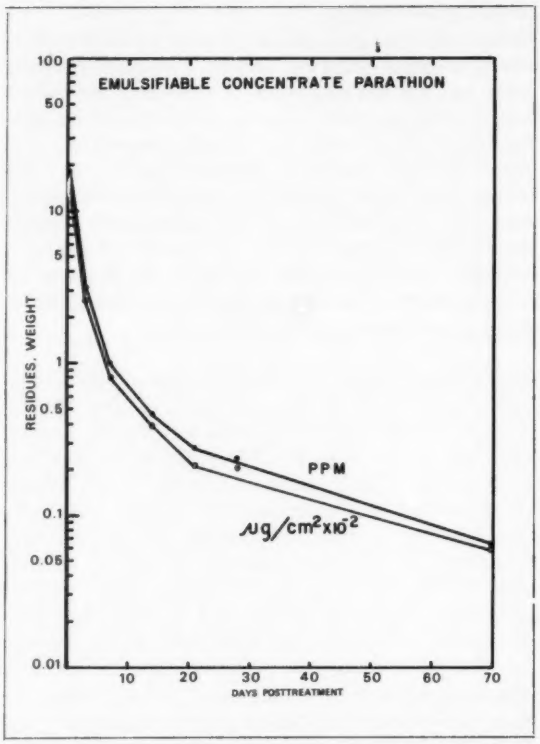

FIGURE 2. *Parathion residues from punched peach leaf samples following application of emulsifiable concentrate formulation at 1 lb a.i./acre*

is extracted with a soluable organic solvent and nearly all the active pesticide is retrieved. Hence the plastic capsule does not act as a barrier between the pesticide and the solvent.

Formulations played a major role in comparing percents of dislodgable residue removed. The percentage of dislodgable residue in the EC formulation from punched samples ranged between 17 and 33 percent with an average of 25 percent for seven sampling periods. The WP formulation gave a higher percent of dislodgable residue and ranged between 43 and 61 percent with an average of 47 percent for seven sampling periods.

Residue levels throughout the growing season degraded as one might expect with EC and WP parathion. With Enc. parathion the degradation as expressed by the slope was flatter, as anticipated. The percentage of dislodgable parathion compared to the remaining residue was considerably higher: about two-thirds of the total residue was dislodgable. Again it should be emphasized that with this particular formulation dislodgable residues include both capsulated and noncapsulated

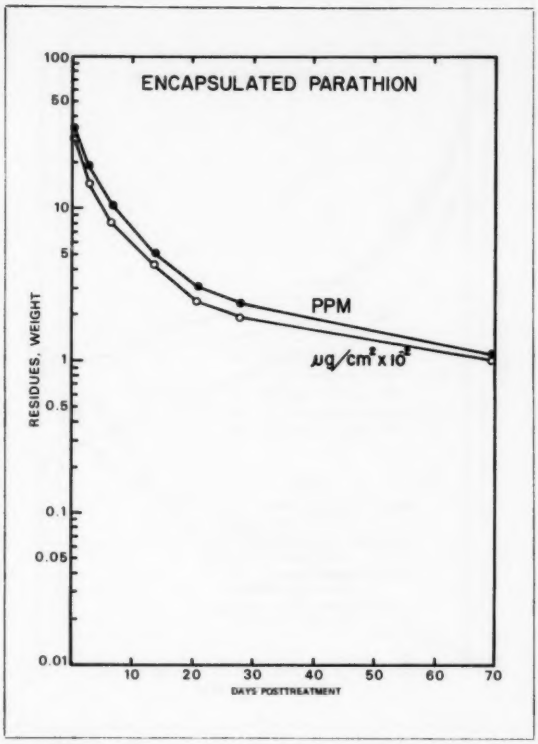

FIGURE 3. *Parathion residues from punched peach leaf samples following application of encapsulated formulation at 1 lb a.i./acre*

forms. What this means in actual exposure through oral and dermal contact cannot be ascertained from this study; additional work is needed to determine whether the parathion is actually in an exposed form. Enc. parathion resulted in punched-leaf residues of 1.12 ppm or 10 µg/cm² at time of harvest. Whole-leaf samples had residues of 0.76 ppm or 7 µg/cm² on 70-day harvest samples.

Paraoxon and the s-ethyl isomer, two potentially toxic degradation products of parathion, were also included in the study. Punched samples were limited so all analyses conducted for these two products are reported for whole-leaf samples only. Figure 7 shows the degradation of paraoxon throughout the 70-day study for each of the three formulations. Analyses were also separated according to their total and dislodgable resi-

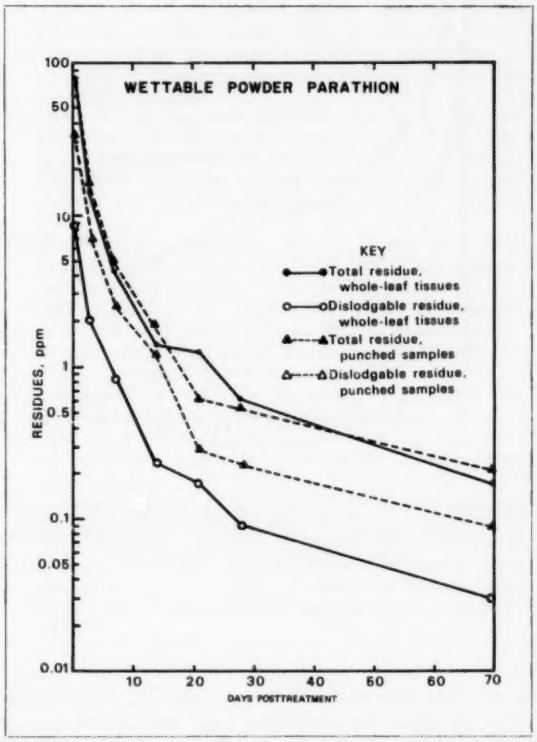

FIGURE 4. *Parathion residues on and in whole peach leaf samples following application of wettable powder formulation at 2 lb a.i./acre*

TABLE 1. *Parathion residues in punched peach leaf samples*

Days Post-treatment	Wettable Powder			Emulsifiable Concentrate			Encapsulated Parathion		
	PPM	$\mu G/CM^2 \times 10^{-2}$	PPM $\mu G/CM^2 \times 10^{-2}$	PPM	$\mu G/CM^2 \times 10^{-2}$	PPM $\mu G/CM^2 \times 10^{-2}$	PPM	$\mu G/CM^2 \times 10^{-2}$	PPM $\mu G/CM^3 \times 10^{-2}$
0	69.5	60.8	1.14	18.4	14.7	1.25	34.9	31.5	1.11
3	16.0	11.4	1.41	3.16	2.64	1.20	19.6	14.6	1.34
7	5.12	41.5	1.23	1.00	0.815	1.23	10.4	8.02	1.30
14	1.88	1.45	1.30	0.47	0.387	1.21	5.18	4.27	1.21
21	0.62	0.488	1.27	0.28	0.214	1.31	3.11	2.48	1.25
28	0.54	0.415	1.30	0.24	0.204	1.18	2.40	1.96	1.22
70	0.20	0.157	1.27	0.065	0.060	1.08	1.12	1.03	1.09
Average			1.27			1.21			1.22
Standard deviation			0.0755			0.0653			0.0852

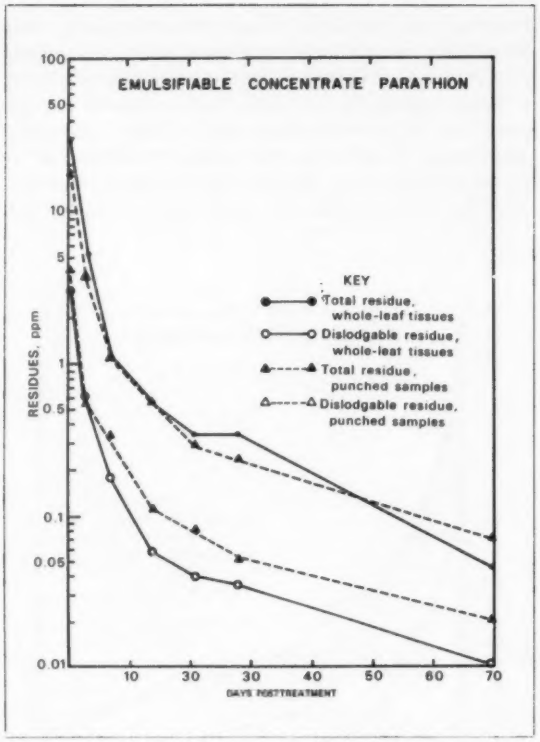

FIGURE 5. *Parathion residues on and in whole peach leaf samples following application of emulsifiable concentrate formulation at 1 lb a.i./acre*

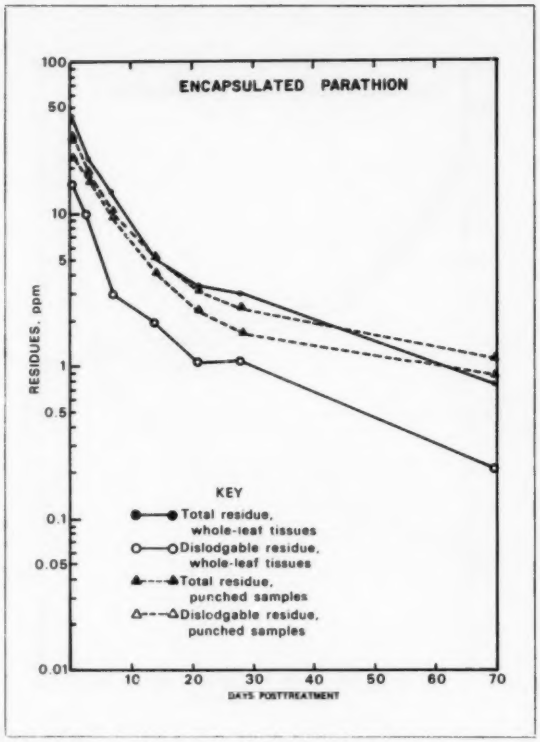

FIGURE 6. *Parathion residues on and in peach leaves following application of encapsulated formulation at 1 lb a.i./acre*

dues. Paraoxon was lowest with the EC formulation and was below the detectable limit the second day of sampling. Samples sprayed with the WP and Enc. formulations contained considerably higher levels of paraoxon than the EC formulation; the rate of degradation was similar to parathion, particularly after the third post-application day. Paraoxon was barely detectable (0.01 ppm) at harvesttime. The greater percentage of paraoxon residue was found in the dislodgable form. This could be attributed to either the fact that paraoxon has greater polarity than parathion, which would make it more extractable in the aqueous solvent, or to the difference in rate of surface degradation compared to metabolic degradation.

The s-ethyl isomer of parathion was detected in only very small quantities the first few days after application of the WP and Enc. formulations and was not at all detectable after the EC applications. Using the Enc. formulation, the residue declined from 0.11 ppm the day of application to 0.04 ppm the third day following application. With the WP formulation, the residue declined from 0.28 ppm to 0.05 ppm during this same period. Nearly all residue from the Enc. application was in the dislodgable form; 50 percent of the WP application was in dislodgable form. This study indicates that residues of the s-ethyl isomer were low enough to be excluded from future studies involving parathion on peach trees.

All dislodgable and remainder residues on harvested fruit samples were less than 0.01 ppm parathion. Neither paraoxon nor the s-ethyl isomer could be found on fruit samples.

Acknowledgment

Authors gratefully acknowledge the assistance of Warren Dow, who supplied the 60 acres of peaches on which this study was conducted. Our thanks go also to Chevron Chemical Company and the Penwalt Corporation, who supplied formulations used in this study.

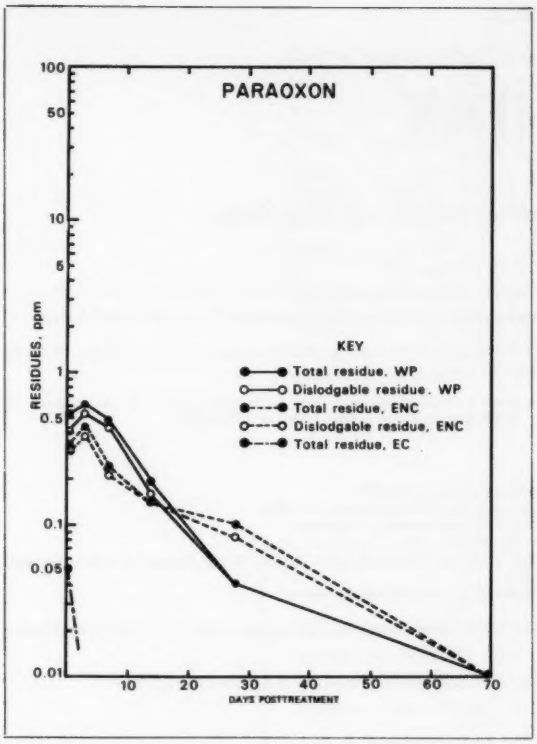

FIGURE 7. *Paraoxon on and in peach leaves following parathion application*

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALDRIN	Not less than 95% of 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene
BHC (BENZENE HEXACHLORIDE)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers). Commercial product contains several isomers of which *gamma* is most active as an insecticide.
CHLORDANE	1,2,3,4,5,6,7,8,8-Octachlor-2,3,3a,4,7,7a-hexahydro-4,7-methanoindane. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomer forms of chlordane.
DDD	See TDE.
DDE	Dichlorodiphenyl dichloro-ethylene (degradation product of DDT) Main component (*p,p'*-DDE): 1,1-Dichloro-2,2 bis(*p*-chlorophenyl) ethylene *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene
DDT	Main component (*p,p'*-DDT): 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl) ethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane]
DIELDRIN	Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethano-naphthalene
ENDRIN	1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene
ETHYLENETHIOUREA	2-Imidazolidinethione
HCB	Hexachlorobenzene
HEPTACHLOR	1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindane
LINDANE	*Gamma* isomer of benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane) of 99+% purity
MALATHION	*S*-[1,2-Bis(ethoxycarbonyl)ethyl] *O,O*-dimethyl phosphorodithioate
METHOXYCHLOR	1,1,1-Trichloro-2,2-bis(*p*-methoxyphenyl) ethane
OXYCHLORDANE	1,2,4,5,6,7,8,8-Octachloro-1,2-epoxy-3a,4,7,7a-tetahydro-4,7-methanoindan
PCB'S (POLYCHLORINATED BIPHENYLS)	Mixtures of chlorinated biphenyl compounds having various percentages of chloride
TDE	1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethane. Technical TDE contains some *o,p'*-isomer also.
TOXAPHENE	Chlorinated camphene (67-69% chlorine). Product is a mixture of polychlorinated bicyclic terpenes with chlorinated camphenes predominating.

ERRATUM

PESTICIDES MONITORING JOURNAL, Volume 7, Number 3/4, p. 139. In the paper "Levels of Mirex and Some Other Organochlorine Residues in Seafood from Atlantic and Gulf Coastal States," a quotation of P. A. Butler's article "Monitoring Pesticide Pollution" [*BioScience, 19(10)*], which stated that mirex was "one of the most abundant of the organochlorine pesticides found in shellfish off the Atlantic, Gulf, and Pacific coasts," was misleading. Butler actually stated, "Although each sample is screened for 10 or more pesticides, DDT (including its metabolites) is the only one commonly present. Dieldrin is next in frequency of occurrence, followed by endrin, toxaphene, and mirex."

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SUBJECT AND AUTHOR INDEXES

Volume 8, June 1974—March 1975

Preface

Primary headings in the subject index consist of pesticide compounds, the media in which residues are monitored, and several concept headings, as follows:

Pesticide Compounds (listed alphabetically by common name or trade name when there is no common name)

Media and Concept Headings

- Air
- Degradation
- Experimental Design
- Factors Influencing Residues
- Food and Feed
- Household Items
- Humans
- Plants (other than those used for food and feed)
- Sediment
- Soil
- Water
- Wildlife

Compound headings are also used as secondary headings under the primary media and concept headings and vice versa.* When a particular paper discusses five or more organochlorines, the compounds are grouped by class under the media or concept headings; in the primary headings, however, all compounds are listed individually. The specific compounds or elements which have been grouped in various combinations by class for certain papers are as follows:

Organochlorines

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DDE
DDMU
DDT
dicofol
dieldrin
endosulfan
endrin
heptachlor
heptachlor epoxide
methoxychlor
mirex
nonachlor
oxychlordane
perthane
Strobane®
TDE
toxaphene

In the author index, the names of both senior and junior authors appear alphabetically. Full citation is given, however, only under the senior author, with a reference to the senior author appearing under junior authors.

* Note: With the exception of 8(2):69-97 and 8(2):110-124 in which no compounds are used as secondary headings.

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